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# HAND-BOOK

OF

# CHEMISTRY.

BY

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## VOL. VI.

## METALS—*(concluded.)*

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# ERRATA.

## VOL. I.

Page Line

160 — 19 from bottom; *for* one, only *read* one only;

195 — 6 from top; *for* Kupfer-lazar *read* Kupfer-lasur

238 — 14 ,, ; *for* pellow *read* yellow

267 — 18 ,, ; *for* atmospheric enclosed *read* atmospheric air enclosed

515 — 11 from bottom; *for* uranim *read* uranium

## VOL. II.

119 — 11 from bottom; *for* Guy-Lussac *read* Gay-Lussac

133 — 18 ,, ; *for* 68 *read* 65

135 — 9 from top; *for* Protophosphide of Hydrogen *read* Solid Phosphide of Hydrogen

162 — 23 ,, ; *for* tetrathionic *read* tetrathionic acid

257 — 16 ,, ; *for* Sulphurous *read* Sulphuric

299 — Heading of page; *for* Hyperchlorites *read* Hypochlorites

318 — 25 from bottom; *for* chlorate *read* chlorite

353 — 15 from bottom; *for* Chlorwasserstoffsäure *read* Chlorwasserstoffsaure

372 — 22 ,, ; *for* Carenwinder *read* Corenwinder

377 — 3 from top; *for* nitric *read* nitrique

472 — 24 ,, ; *for* lead-paint *read* lead-plaster

475 — 4 ,, ; *for* Möhler *read* Wöhler

503, 504. In Table IV; *for* Atmosphere *read* Atmospheres

## VOL. III.

19 — 5 from bottom; *for* paper-cone *read* conical iron crucible

238 — 6 from top; *for* Phil. Mag. Ann. *read* Phil. Mag. J.

## VOL. V.

127 — 4 from bottom; *for* $\frac{1}{8000}$ and $\frac{1}{5000}$ *read* $\frac{1}{8000}$ and $\frac{1}{5000}$

175 — 13 ,, ; *for* diaphareticum *read* diaphoreticum

# METALS,

(*Continued.*)

## Chapter XXXVI.

# MERCURY.

Zaboada. *J. Phys.* 60, 378.
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H. Rose.—Behaviour of Mercurial Salts with Sulphuretted Hydrogen. *Pogg.* 13, 59. Behaviour of Mercurial Salts with Phosphuretted Hydrogen. *Pogg.* 40, 75. Salts of Mercurous Oxide. *Pogg.* 51, 117.
Kane.—Salts, Ammonia-compounds, and Amidogen-compounds of Mercury. *Ann. Chim. Phys.* 72, 215.
Marignac.—Mercurous Nitrates. *N. Ann. Chim. Phys.*
Gerhardt.—Mercurous Nitrates.

Synonymes. *Quicksilver, Quecksilber, Mercure, Mercurius, Hydrargyrum, Argentum vivum.*

*History.*—Known from the earliest times. Cinnabar was used as a pigment by the ancients; corrosive sublimate was known to the Arabians, and calomel to the alchemists.

*Sources.* Often found native; more frequently as sulphide, either alone, in the form of cinnabar, or mixed with Idrialine, in Quicksilver Liver-ore and Brand-ore, and also in some varieties of Fahl-ore; very rarely as selenide of mercury, combined with sulphide of mercury, selenide of zinc, or selenide of lead; as iodide and chloride of mercury, and likewise combined with silver, in native Amalgam. Common salt appears also to contain traces of mercury, inasmuch as (according to Rouelle, *J. de Médec.* 48, 299, Proust, *Scher. J.* 4, 190, Westrumb, *kl. phys. chem. Abhandl.* 4, 1, 423, and Wurtzer, *Schw.* 37, 83), when it is distilled with oil of vitriol, corrosive sublimate sometimes passes over together with the hydrochloric acid; the mercury may, however, have been contained in the oil of vitriol.

*Preparation.* By distilling mercurial ores in contact with lime, smithy-scales, or common air, so as to remove the sulphur by formation of sulphide of calcium, sulphide of iron, or sulphurous acid; partly also to remove chlorine. In the Bavarian Rheinpfalz, a mixture of ore and lime is heated to redness in long cast-iron bottles, placed in nearly horizontal rows one above the other, in a long furnace, and provided with receivers. At Horowitz, in Bohemia, a mixture of ore and smithy-scales is placed in iron dishes, which are attached one above the other by the centres of their bases to a vertical iron axis, and covered over with an iron receiver, closed at top, and dipping into water at bottom. The upper part of the receiver is surrounded by the furnace, and imparts its heat to the dishes, from which the mercury rises in vapour, and collects in the water contained in the trough. This process is called *Distillatio per descensum.* At Idria in Illyria, the quicksilver-ore, coarsely broken up, is laid upon a perforated stone arch in a turret-shaped furnace, and, after the apertures by which it is introduced have been stopped, heated to redness by flames made to play against the under surface of the arch. The sulphur is burnt by the air, which is admitted through channels constructed for the purpose; and the mixture of mercurial vapour, sulphurous acid, and smoke from the furnace, is made to pass through a horizontal channel constructed in the upper part of the furnace, then up and down through seven condensing chambers, and finally through a turret-shaped chamber into the air. In the course of this long transit, the mercury condenses in the chambers, the floor of which, being inclined to one side, enables it to run out; it is then collected, and strained through coarse cloth. A similar process is followed at Almaden in Spain, excepting that the vapours, instead of passing through condensing chambers, are made to traverse a series of tubes made up of cylinders, called *Aludels*, open at both ends, and fitting one into the other. These are laid upon a surface, called the *Aludel-bath*, first descending a little, and then ascending, and finally open into the chimney.—Mercury is sent into the market, sometimes in leathern bags, and sometimes in wrought-iron bottles, which are afterwards used in chemical laboratories for the preparation of potassium.

*Purification from foreign metals.* 1. The mercury is distilled, either alone, or, better, under a thick layer of iron filings, in glass, earthen, or other retorts. A portion of the foreign metals is very apt to pass over with the mercury, either in the form of vapour or by spirting during the ebullition. The latter of these accidents is prevented by a coating of iron-filings.—2. By distilling the mercury with one-tenth of its weight of cinnabar, the sulphur of which retains the foreign metals. (Dörfurt.)

3. By distilling cinnabar prepared by sublimation (or corrosive sublimate) with one part of lime or iron-filings. This method yields the purest mercury, because, in the preparation of the cinnabar, the sulphides of the foreign metals remain unsublimed.—4. By distilling red oxide of mercury. The metal thus obtained is covered with a film of reproduced oxide, and appears dingy and sluggish of motion. From these defects it may be freed by agitation with dilute nitric acid, or with warm dilute sulphuric acid. (Mohr, *Ann. Pharm.* 25, 222.)—5. By boiling a solution of corrosive sublimate in a clean iron vessel. (Voigtel.)—6. By boiling the impure mercury for some hours with $\frac{1}{87}$ of its weight of mercurous nitrate dissolved in water, or with a small quantity of very dilute nitric acid. [According to Wittstein (*Repert.* 65, 362) the boiling with solution of corrosive sublimate, as above mentioned, is disadvantageous, because it occasions the formation of calomel.] Or by agitating the mercury for some days with sulphuric acid—which must be stronger, as the mercury is more impure—till the acid no longer becomes turbid, or takes up any foreign substance. (Branchi, *Repert.* 6, 77.)—¶ 7. Ulex agitates 2 pounds of mercury with half an ounce of solution of sesquichloride of iron, having a specific gravity of 1·48. The mercury is thereby reduced to a state of very fine division, and the action on the foreign metals is accelerated by the formation of chloride of mercury, which collects between the drops. It is sufficient to agitate the mercury with the iron solution for ten minutes, and then wash it with water. The mercury, after drying, is easily reunited by the application of a gentle heat. (*Ann. Pharm.* 60, 210.)¶—Pure mercury should leave no residue when dissolved in nitric acid, evaporated, and ignited; or when fused with sulphur and sublimed in a glass flask. When made to run down a gently-inclined surface, it should retain its round form, and *not leave a tail;* and when agitated in a bottle with dry air, it should not yield any black powder.

*Properties.* Mercury freezes, according to Hutchins, at $-39{\cdot}44°$, undergoing considerable contraction, and forming a tin-white, ductile mass, crystallized in octohedrons and needles, capable of being cut with a knife, and exhibiting a granular fracture. At ordinary temperatures, it forms a very coherent but very mobile liquid, which adheres but slightly to glass, and has a density of 13·5592 (Karsten), 13·5886 at 4°, and 13·535 at 26° (Kupffer), 13·568 (Cavendish and Brisson), 13·575 (Fahrenheit), 13·613 at 10° (Biddle), 13·595 at 4° (Kopp), 13·596 (Regnault). Mercury remains unaltered when agitated for any length of time with oxygen gas, common air, hydrogen, nitrogen, nitrous oxide, nitric oxide, carbonic acid gas, or alcohol; but any foreign metals that may be mixed with it, become oxidized by agitation in air or oxygen gas, producing a grey pulverulent mixture of the oxides of the foreign metals and finely divided metallic mercury. On the other hand, by agitation with water, ether, or oil of turpentine, or by trituration with sulphur, sulphide of antimony, sugar, grease, &c., even in vacuo, mercury is converted into a grey powder, *Æthiops per se*, consisting of small globules of the metal, which are separated by interposition of foreign matter, but run together again on its removal: *Extinction, Deadening of Mercury.* (Brugnatelli, Proust, *A. Gehl.* 6, 394; A. Vogel, *Ann. Chim.* 58, 171; 74, 220; further, *Schw.* 4, 393; Roux, *J. Pharm.* 11, 215.) In well prepared grey mercurial ointment, the mercury forms nearly uniform globules having a diameter between $\frac{1}{500}$ and $\frac{1}{1000}$ of a line, and not distinguishable by the naked eye. (Ehrenberg, *Pogg.* 24, 40.) The deadening

of quicksilver was formerly attributed to oxidation. ¶ According to Bärensprung (*J. pr. Chem.* 50, 21), some, at least, of the mercury in grey mercurial ointment is in the state of black oxide (the quantity being greater, the older the ointment), and this oxide, after the fat has been extracted by ether, may be dissolved out by water slightly acidulated with sulphuric acid. ¶ Mercury boils, according to Crichton, at 346°; according to Dalton, at 349°; according to Heinrich, at 356°; according to Dulong & Petit, at 360°, and is thereby converted into a colourless vapour. Vapour rises, however, from mercury, even between + 15·5° and 27° (but not at — 6·7°), both in vacuo and in spaces filled with air, as shown by the silvering of gold-leaf, kept for two months in a vessel over mercury. (Faraday, *Schw.* 32, 482; and *Pogg.* 9, 7°.) ¶ According to Karsten (*Pogg.* 71, 245), mercury at temperatures below 0°, gives off sufficient vapour to bring out the image on a Daguerreotype plate held over it. Brame (*Instit.* 1849, 403) finds that sulphur in the very finely divided, utricular condition (*utricules de soufre*) in which it is first precipitated from the state of vapour, is a much more delicate test for the presence of mercurial vapour than gold-leaf. By means of this test, he finds that at 12°, the vapour of mercury rises to a height of more than a metre; that even at 8°, it appears to have no limited atmosphere; that it rises, at ordinary temperatures, from amalgams and mercurial ointment; that in presence of air and sulphur-vapour, it diffuses, according to the same law as other gases; but that in presence of air and iodine-vapour, and of the vapour of iodide of mercury thereby produced, the law of diffusion appears to be different. ¶ The following observation appears likewise to be connected with this subject. Some mercury, forming part of the cargo of a ship on the Spanish coast, ran out of the bags, which had become rotten, and found its way into the hold, where it mixed with the bilge-water. An elastic fluid was in consequence evolved, which covered every piece of metal in the vessel with a coating of quicksilver, and affected the whole ship's company with violent symptoms of salivation. (Burnett, *Phil. Trans.* 1823, 402; abstr. *Gilb.* 40, 347.)

## *Compounds of Mercury.*

All compounds of mercury are either volatilized or decomposed by heat, and yield metallic mercury when distilled with carbonate of soda. The mixture should be slightly moistened, otherwise a portion of chloride or bromide of mercury may sublime undecomposed.

Atomic weight of mercury: 101·2658 (Berzelius); 100·04 = 100 (Erdmann & Marchand, *J. pr. Chem.* 31, 392).

According to Wiggers (*Pogg.* 41, 440), mercury is slightly soluble in boiling water. When 20 ounces of water are poured upon 2 ounces of mercury, and boiled down to 10 ounces, the decanted liquid shows no particular reaction with sulphuretted hydrogen or protochloride of tin; but on mixing it with 10 drops of nitric acid, and evaporating, the residue exhibits a slight brown tint when treated with sulphuretted hydrogen. Anthon also (*J. pr. Chem.* 15, 153) found that water boiled with mercury for 15 hours, and then decanted, was capable of silvering gold-leaf; and after evaporation with nitric acid, gave the characteristic reactions with sulphuretted hydrogen and protochloride of tin. Paton and Favrot (*J. Chim. méd.* 14, 306), in repeating the experiment of Wiggers with

distilled water and with river-water, did not discover mercury in the water after evaporation with nitric acid: Girardin also (*J. Chim. méd.* 9, 283), found no mercury in water which had been boiled with that metal; he did not, however, mix it with nitric acid before evaporation. When water is poured upon mercury, boiled down to one-half, decanted, then left to stand for several days, again decanted, and thrown upon a thick paper filter, small quantities of mercury, sufficient to silver gold-leaf, remain on the filter; but the filtrate, when mixed with nitric acid and evaporated, shows no trace of mercury. Perhaps the quantity used in the experiment was too small; but, at all events, the experiment shows that the mere decantation adopted by Wiggers is not sufficient to separate the water from the mercury mechanically mixed with it; to decide the question completely, experiments should be made with larger quantities of water. (Gm.)

## Mercury and Oxygen.

### A. Mercurous Oxide. $Hg^2O$.

*Di-oxide of Mercury, Sub-oxide of Mercury, Black Oxide of Mercury, Quecksilberoxydul, Schwarzes Quecksilberoxyd, Protoxide de Mercure, Oxyde mercureux.*

This oxide is formed, in combination with acids, by the action of nitric or sulphuric acid, not very strongly heated, on excess of mercury; also by heating dissolved mercuric salts with metallic mercury.

*Preparation.* By decomposing a mercurous salt or the dichloride of mercury with an aqueous fixed alkali in excess; the separated mercurous oxide must be washed and dried in the dark. Donovan diffuses finely pounded dichloride of mercury in water, treats it at once with excess of potash, and then washes and dries the product. The mercurous oxide thus obtained, yields but few globules of mercury on trituration. If too little potash be added in the first instance, there is formed, according to Donovan, a basic hydrochlorate of mercurous oxide, which abstracts oxygen from the separated oxide, and is itself converted into basic hydrochlorate of mercuric oxide, so that a further addition of potash produces a mixture of dioxide, protoxide, and metallic mercury. Duflos (*N. Br. Arch.* 23, 310) adds 1 part of caustic potash-ley to 12 parts of absolute alcohol—decants the liquid from the resulting precipitate—mixes $\frac{1}{12}$ of it with a solution of mercurous nitrate (stirring constantly), till the liquid slightly reddens litmus—then adds the remaining $\frac{1}{12}$—leaves the precipitate to subside—decants—washes it with water—and dries it at a gentle heat in the dark. The mercurous oxide thus obtained is black, with a tinge of yellowish brown, gives up nothing to dilute hydrochloric acid, but dissolves completely in strong acetic acid. According to Guibourt (*Ann. Chim. Phys.* 1, 422), it is impossible to obtain this oxide pure, because, during washing, even in the dark, it is resolved into a mixture of the protoxide with metallic mercury. The product formed by triturating the protoxide with mercury is merely a mixture.

*Properties.* Brown-black powder, destitute of taste and smell. Specific gravity of that obtained from calomel by the action of caustic potash, 8·9503 (Karsten), 10·69 (Herapath).

| | | | Sefström. | | Fourcroy & Thénard. | | Donovan. | | Guibourt. |
|---|---|---|---|---|---|---|---|---|---|
| 2Hg | 200 | 96·15 | 96·2 | | 96·16 | | 96·04 | | 95·69 |
| O | 8 | 3·85 | 3·8 | | 3·84 | | 3·96 | | 4·31 |
| $Hg^2O$ | 208 | 100·00 | 100·0 | | 100·00 | | 100·00 | | 100·00 |

| | Zaboada. | Braamcamp & Siqueira Oliva. | Chenevix. |
|---|---|---|---|
| Hg | 95 | 92·5 | 89·3 |
| O | 5 | 7·5 | 10·7 |
| | 100 | 100·0 | 100·0 |

($Hg^2O = 2 \cdot 1265{\cdot}823 + 100 = 2631{\cdot}646$. Berzelius.)

*Decompositions.* Light, even diffused daylight, or a gentle heat, resolves the dioxide of mercury into metallic mercury and the protoxide, (at 100° according to Donovan; according to A. Vogel, however, *Ann. Chim.* 84. 221, the decomposition does not take place at that temperature). At a red heat, it is resolved into mercury and oxygen gas. By aqueous phosphorous acid, it is converted into mercury and phosphoric acid. (Braamcamp & Siqueira Oliva.) By potassium and sodium, at about the melting points of those metals, it is decomposed, with vivid ignition and slight detonation, yielding metallic mercury and an alkali. (Gay-Lussac & Thénard.) Detonates when struck with phosphorus.—It is slowly decomposed by phosphuretted hydrogen gas. (Graham.)—Boiled with aqueous iodide of potassium, it yields metallic mercury and protiodide of mercury and potassium; if the mercurous oxide is in excess, diniodide of mercury is formed at the same time. (Berthemot, *J. Pharm.* 14, 189.) A concentrated solution of sal-ammoniac decomposes it in a similar manner, ammonia being evolved, and mercury and hydrochlorate of mercuric oxide separated. (Pagenstecher, *Répert.* 27, 27; L. Thompson, *Phil. Mag. J.* 10, 179.)—Carbonate of ammonia likewise decomposes mercurous oxide into mercuric oxide which dissolves, and metallic mercury which remains behind. (Wittstein.)

*Combinations.* With acids, forming the Salts of Mercurous Oxide, or Mercurous Salts.—These salts are obtained, either by dissolving mercury in excess in certain oxidizing acids, such as nitric or sulphuric acid, or by dissolving mercurous oxide in acids; or by double decomposition.—The basic salts are mostly yellow, the normal salts white; most of them are soluble in water, redden litmus, and have a metallic taste; their action on the human body is not very violent. Some of the normal salts are resolved by water into acid salts which dissolve, and basic salts which remain undissolved.

Mercurous salts are decomposed, with precipitation of metallic mercury, by the following substances:—*By charcoal.* This substance, when immersed in a solution of mercurous nitrate, becomes covered, in the course of two days, with globules of mercury. (Boeck.)—*By phosphorus.* Phosphorus immersed in mercurous nitrate, soon becomes covered with mercury. (Boeck, Fischer.)—*By phosphorous and hypophosphorous acids.* These acids, added to mercurous salts, throw down finely-divided mercury. (Braamcamp & Siqueira Oliva.) Characters traced on paper with the mercurous solution, assume a metallic aspect when the paper is kept in a bottle containing phosphorus. (Grotthuss.)—*By sulphurous acid.* This acid, added to a solution of mercurous nitrate, immediately throws down metallic mercury as a blackish-grey powder; but even when the sulphurous acid is in excess, a portion of the mercury remains in solution for

several days, and is precipitated by boiling. (A. Vogel.)—*By zinc, cadmium, iron, tin, lead, bismuth, copper, antimony,* and *arsenic.* Zinc, cadmium, lead, copper, and bismuth, immersed in solution of mercurous nitrate, throw down the whole of the mercury in 24 hours; the other metals leave a portion of the mercury in solution. Iron exerts no action, [because it becomes passive]. Sometimes a white or yellow precipitate is formed at the same time; this precipitate, in the case of zinc, cadmium, and copper, consists of basic mercurous nitrate; with bismuth, of monobasic bismuth-nitrate; with lead, of basic mercurous nitrate and lead-nitrate together. Tin becomes covered with a brown, and antimony with a yellowish brown powder, which continually deepens in colour, and, after a few days, is resolved into globules of mercury. (Fischer, *Pogg.* 9, 258.) Mercury is likewise reduced from mercurous salts by brass, and by the alloys of silver with zinc, tin, lead, and copper,—by the latter, even when it contains 3 parts of silver to one of copper. (Fischer, *Pogg.* 12, 504.)—Iron and arsenic also decompose mercurous salts at ordinary temperatures. (Orfila, *J. Chem. méd.* 6, 321.)—Iron produces no precipitate in a very concentrated solution of mercurous nitrate, because it becomes passive; but from a dilute solution of that salt, and likewise from the acetate, it readily throws down metallic mercury. (Gm.) —Copper immersed in the mercurous solution, becomes covered with a grey film, which assumes a silver-white aspect on being rubbed between paper.—*By protochloride of tin.* This reagent precipitates dichloride of mercury, which is immediately converted into metallic mercury. (Soubeiran.)—*By green vitriol.* (Keir, *Schw.* 53, 166; Orfila.) This salt, added to mercurous nitrate, thrown down a white powder consisting of mercurous sulphate, which soon turns grey and is converted into globules of mercury. (Gm.)—*By certain organic compounds.* Sugar, boiled with mercurous acetate, throws down metallic mercury, together with a small quantity of dioxide. (A. Vogel.) Oil of turpentine reduces mercury from mercurous salts. (Orfila.)—Hydrocyanic acid, added to mercurous salts, throws down half the mercury and forms cyanide of mercury:—

$$Hg^2O + HCy = Hg + HgCy + HO.$$

Hydrosulphuric acid and alkaline hydrosulphates yield, with mercurous salts, a black precipitate of disulphide of mercury. The precipitate is black, even when the quantity of the reagent is insufficient for complete precipitation. It is insoluble in excess of ammonia or hydrosulphate of ammonia. (H. Rose, *Analyt. Chemie.*) Not a trace is dissolved, even with the aid of heat; but if the hydrosulphate of ammonia contains excess of sulphur, the black precipitate is converted into protosulphide. (Gm.) It dissolves in excess of the alkaline hydrosulphate, with separation of metallic mercury (?). (Mialhé, *N. Ann. Chim. Phys.* 5, 170.) Dissolves in caustic potash, with separation of metallic mercury; acids added to the filtrate throw down protosulphide of mercury. (H. Rose.) Absolute alcohol, united with 6 volumes of sulphuretted hydrogen, has no action on dry mercurous salts. (Parnell.)—Free trithionic acid forms a black precipitate with mercurous salts (Langlois); tetrathionic and pentathionic acids give yellow precipitates, which blacken on boiling. (Kessler.)—Alkaline hyposulphites throw down sulphide of mercury, sulphuric acid remaining in the liquid. (H. Rose, *Pogg.* 33, 241.)—Hydriodic acid and iodide of potassium throw down green diniodide of mercury:—

$$Hg^2O,NO^5 + KI = Hg^2I + KO,NO^5.$$

The precipitate is soluble in excess of iodide of potassium.—Hydrobromic acid and bromide of potassium give white precipitates with mercurous salts.—Hydrochloric acid and soluble metallic chlorides added to these salts, throw down dichloride of mercury. If the solution is somewhat concentrated, the precipitate is curdy; in dilute solutions, it takes the form of a fine powder; and in case of great dilutions, only an opalescence is produced; this last effect is visible even to the 80,000th degree of dilution. (Pfaff.) The precipitate is scarcely soluble in excess of the reagent; it turns black when treated with potash or ammonia.

Caustic alkalis added to mercurous salts, yield a black precipitate of mercurous oxide. When ammonia is used, the precipitate generally contains more or less of the newly formed salt.—¶ According to Lefort, (*N. J. Pharm.* 8, 5), the precipitate formed by caustic alkalis in mercurous salts, always amalgamates gold-leaf, and must therefore be regarded as a mixture of mercuric oxide with metallic mercury.—¶ Monocarbonate of potash forms a yellow, and bicarbonate of potash a white precipitate, of mercurous carbonate, which is slightly soluble in excess of the alkaline carbonate, and when boiled, gives off carbonic acid and turns black.—Very small quantities of carbonate of ammonia form a grey, and larger quantities a black precipitate. The carbonates of baryta, strontia, lime, and magnesia, precipitate mercurous salts, even in the cold. (Demarçay.)—Phosphate of soda forms a white precipitate of mercurous phosphate; according to Pfaff, to the 10,000th degree of dilution.—Alkaline chromates yield a bright brick-red precipitate of mercurous chromate.

Oxalic acid forms a white precipitate of mercurous oxalate. So likewise do alkaline oxalates, up to the 10,000th degree of dilution. (Pfaff.)—Ferrocyanide of potassium produces a thick white precipitate, and ferricyanide of potassium a red-brown precipitate, which turns white after standing for some time.—Tincture of galls yields a brownish yellow precipitate with mercurous salts.—Most mercurous salts, which are insoluble of water, dissolve in nitric acid.

## B. Mercuric Oxide. HgO.

*Protoxide of Mercury, Red oxide of Mercury, Quecksilberoxyd, Rothes Quecksilberoxyd, Deutoxyde de Mercure, Oxyde mercurique.*

*Formation.* 1. Mercury heated to the boiling point for a considerable time in contact with the air, is converted, without visible combustion, into mercuric oxide.—When the two poles of Hare's deflagrator are made to dip into two vessels full of mercury, and the mercury allowed to run in a fine stream through a narrow opening from the upper to the lower vessel, visible combustion takes place, according to Hare. The blue light which is seen whenever the circuit of a powerful galvanic battery is closed by dipping the connecting wire into mercury, is likewise due to combustion of the mercury.—2. This oxide is also formed when the metal is heated with excess of nitric or sulphuric acid.

*Preparation.* 1. By keeping mercury for a month or longer at a boiling heat in a flask filled with air, and having a long loosely-fitting tube adapted to its mouth: *Mercurius præcipitatus per se.*—2. By exposing the nitrate of mercuric or mercurous oxide to a high and gradually increasing

temperature in a crucible, or, better, in a glass vessel surrounded with sand as long as nitrous acid is evolved. To save nitric acid, the oxide, moistened with water, may be previously triturated with an equal weight of mercury, till the latter is completely deadened: *Mercurius præcipitatus ruber*. Care must be taken not to raise the temperature too high. The oxide prepared by this process on the small scale is a dull powder; in commerce, it occurs in shining crystalline grains. According to Gay-Lussac, the small unpulverized crystals of mercurous nitrate yield the second form of the oxide, but the pulverized salt yields the first form. The more perfect crystallization of the oxide prepared on the large scale is undoubtedly due to the slower rate at which the heat increases. According to Winckler (*Répert.* 31, 475) the commercial oxide likewise contains 2 per cent. of nitre, which probably exerts some influence also; it does not, however, appear to be essential, since the oxide prepared by (1) likewise takes the form of crystalline grains.—3. By precipitating a dissolved mercuric salt with excess of potash, and washing the precipitate.

*Impurities.* 1. *Basic nitrate of mercuric oxide*, when the salt has not been sufficiently heated. The oxide containing this salt gives off nitrous vapours when gently heated in a retort. It may be purified in this manner, or by boiling with dilute potash-ley, or by washing with water.—2. *Nitre.* May be completely removed by boiling water. (Winckler.)—3. *Minium.* Remains in the form of fused protoxide of lead, when the mercuric oxide is strongly heated in a glass tube, or in the form of peroxide of lead, when the mercuric oxide is dissolved in nitric acid.—4. *Brick-dust.* Remains behind, when the oxide is ignited or dissolved in nitric acid.—5. *Cinnabar.* Remains, when the oxide is dissolved in hydrochloric acid.

*Properties.* Specific gravity: 11·000 (Pol. Boullay), 11·074 (Herapath), 11·1909 (Karsten), 11·29 at 4° in vacuo (Royer & Dumas), 11·136 (Playfair & Joule). Crystallizes in obtuse rhombohedrons. Such at least was the form in which it was found in a glass containing *Aqua phagadænica* (a mixture of lime-water and protochloride of mercury). (Saladin, *J. Chim. méd.* 7, 530). It is generally crystallo-granular and scaly, shining, and of a bright brick-red colour; by pulverization it acquires an orange yellow colour, lighter as the powder is finer. When prepared on the small scale, it is a dull, flocculent, earthy mass or powder, of a brownish brick-red colour. When obtained by precipitating a mercuric salt with an alkali, it forms a light orange-yellow powder.—When heated, it becomes vermilion-red, and afterwards violet-black, but recovers its original colour on cooling. Has a repulsive metallic taste, and is a violent acrid poison.

Pelouze (*Compt. rend.* 16, 50) supposes that ordinary crystallo-granular mercuric oxide differs from that precipitated by potash (3) in this respect, that the former is crystalline, the latter amorphous. To this he attributes the difference in their chemical properties. When equal quantities of these two oxides are ignited in the same muffle, the amorphous oxide volatilizes completely in a time in which the decomposition of the crystalline oxide is scarcely begun. Dry chlorine gas acts very slowly at ordinary temperatures on the crystalline oxide (hypochlorous acid being produced), and not much more quickly when the oxide is pulverized; but on the precipitated oxide (3) it acts with such violence that the substance becomes red-hot; even when the oxide (3) has been previously heated to a temperature between 300° and 400°, it acts on dry chlorine in the course of a few minutes. (Pelouze).—This view is contradicted by the

following experiments of Gay-Lussac. (*Compt. rend.* 16, 309). When equal quantities of the oxide (1) prepared by boiling mercury in contact with air, and of that precipitated by potash (3) are gradually heated in two glass tubes immersed together in a fused metallic alloy—then cooled —then heated again, and so on,—both oxides begin to give off oxygen at the same temperature, and both cease to evolve it at the same degree in cooling. It is true that (3) gives off rather more oxygen in the same time; but if (1) is previously pounded, the difference is but slight.—Dry chlorine gas produces much less hypochlorous acid with (1) than with (3); but the difference is to be attributed to the much smaller surface which (1) presents, that surface quickly becoming covered with chloride of mercury; the slowness of the action also precludes the rise of temperature by which the decomposition is accelerated in the case of (3). Under water, the two oxides are acted upon by chlorine in the same manner, because the chloride of mercury then dissolves as it forms. Hence it may inferred that the oxide (3) is not amorphous, but in a finely divided crystalline state.

| | | Seftström. | Erdmann & Marchand. | Fourcroy & Thénard. | Donovan. |
|---|---|---|---|---|---|
| Hg | 100 | 92·59 | 92·68 | 92·596 | 92·4 | 92·75 |
| O | 8 | 7·41 | 7·32 | 7·404 | 7·6 | 7·25 |
| HgO | 108 | 100·00 | 100·00 | 100·000 | 100·0 | 100·00 |

| | Proust. | N. Rose. | Zaboada, Braamcamp, & Siqueira Oliva. | Chenevix. |
|---|---|---|---|---|
| Hg | 92 | 91 | 90 | 85 |
| O | 8 | 9 | 10 | 15 |
| | 100 | 100 | 100 | 100 |

*Decompositions.* Mercuric oxide gradually turns black when exposed to sunshine, being superficially decomposed into oxygen and metallic mercury, according to Guibourt, or, according to Donovan, into oxygen and mercurous oxide. At a red heat, it volatilizes completely, being resolved into oxygen gas and vapour of mercury. Part of the mercurial vapour again takes up oxygen, and the oxide thus formed collects on the surface of the mercury which passes over, and diminishes its fluidity. With phosphorus, mercuric oxide detonates under the hammer. Boiled with phosphorus and water, it yields phosphide of mercury and aqueous phosphoric acid (Pelletier); at ordinary temperatures, the same mixture yields fluid mercury and phosphoric oxide, no phosphoric or phosphorous acid dissolving in the water. (Braamcamp & Siqueira.) A phosphate is likewise formed at the same time. (Gm.) Aqueous phosphorous acid forms mercury and aqueous phosphoric acid. (Braamcamp & Siqueira.) Mercuric oxide mixed with sulphur, and heated in a retort, produces a tremendous explosion. (Proust, *Gilb.* 25, 175.) Concentrated sulphurous acid boiled with this oxide, immediately converts it into fluid mercury, with formation of sulphuric acid. At ordinary temperatures, smaller quantities of sulphurous acid produce a rise of temperature amounting to 7·5°, and form a white powder, consisting of mercurous sulphate, part of which dissolves in the liquid. An excess of sulphurous acid turns this powder grey, and reduces it very slowly, but completely, to metallic mercury. So long as this change remains incomplete, the liquid still retains mercury, but is not rendered turbid by addition of common salt; nevertheless, it gives a precipitate with hydrosulphate of ammonia, and after

long standing, or immediately on boiling, deposits metallic mercury in the form of a grey powder; the precipitation of the mercury is complete, provided the quantity of sulphurous acid is not too small. (A. Vogel, *J. pr. Chem.* 29, 273.) Potassium or sodium heated to the melting point, decomposes mercuric oxide with vivid combustion and slight detonation, yielding metallic mercury and alkali. (Gay-Lussac & Thénard.) Zinc and tin filings, and pulverized antimony, heated with mercuric oxide, likewise occasion fiery decomposition. Solution of protochloride of tin poured upon mercuric oxide reduces it to the metallic state, and is itself converted into bichloride, part of which is precipitated in the form of a basic salt, the action being attended with a rise of temperature amounting to 60°. (A. Vogel, *Kastn. Arch.* 23, 80.) Hydrated ferrous oxide converts mercuric into mercurous oxide; so likewise do ferrous salts. (Duflos, *Schw.* 65, 115.) Heated solution of sugar reduces mercuric to mercurous oxide. (A. Vogel.) Chlorine gas decomposes mercuric oxide at a red heat, the products being oxygen gas and protochloride of mercury; at lower temperatures, hypochlorous acid and protochloride of mercury are formed. The latter sometimes combines with the excess of oxide, forming mercuric oxychloride. When dry chlorine gas is passed over the precipitated oxide (3), the heat rises to redness, and oxygen gas is evolved (Pelouze); but if the oxide is surrounded with a freezing mixture (Pelouze) or mixed with a large quantity of sand or sulphate of potash, to prevent the temperature from rising too high, hypochlorous acid is obtained. This acid is likewise produced by the action of chlorine on the precipitated oxide (3), previously heated to between 300° and 400°, or upon the oxide (1) or (2), because in either of these cases the action is slower. Hypochlorous acid is also formed when chlorine gas is passed through water in which mercuric oxide is diffused. (*Vid.* II. 294, 295.) At the boiling heat, according to Braamcamp & Siqueira, a solution of protochloride of mercury and mercuric chlorate is produced.

*Combinations.* *a.* With Water.—¶. *a.* Hydrated Mercuric Oxide.—According to Schaffner (*Ann. Pharm.* 51, 181), the yellow precipitate formed by potash in solutions of mercuric salts is a hydrate containing 3 atoms of water.

| | | | | | Schaffner. |
|---|---|---|---|---|---|
| HgO ..... | 108 | ..... | 80 | ..... | 79·77 |
| 3HO ..... | 27 | ..... | 20 | ..... | 20·23 |
| HgO + 3Aq..... | 135 | ..... | 100 | ..... | 100·100 ¶ |

*β.* Aqueous Mercuric Oxide.—Mercuric oxide is slightly soluble in water (Thomson); the solution tastes strongly metallic; turns violet-juice green; becomes covered, when exposed to the air, with shining films of metallic mercury; is turned brown by hydrosulphuric acid (Guibourt); and exhibits a milky turbidity when mixed with slightly diluted ammonia, which forms a less soluble compound with mercuric oxide. (Guibourt, Donovan.) This somewhat contested solubility of mercuric oxide in water is established by the following observations:—The oxide (2) obtained by the use of nitric acid, and the precipitated oxide (3) dissolve sparingly in cold, somewhat more abundantly in hot water. (Anthon, *Repert.* 58, 305.) When the oxide (2) prepared with nitric acid is used,—having first been completely freed from nitric acid, either by exposure to a degree of heat sufficient to resolve a considerable quantity of the oxide into mercury and oxygen, or by long boiling with caustic potash—

the water still continues to take up the oxide, even after the boiling has been repeated twenty times. (Marchand, *Pogg.* 42, 459.) But even the oxide prepared by (1), the solubility of which cannot well be due to the presence of an acid, yields with water at 10°, a liquid which turns violet-juice green, but does not give a brown colour with hydrosulphate of ammonia; the solution obtained with boiling water turns reddened litmus tincture blue, and becomes brown when treated with hydrosulphate of ammonia. (Boudet, *J. Pharm.* 24, 253; also *J. pr. Chem.* 14, 248.) The same result was obtained by Gossman, (*Repert.* 61, 312, before Boudet), and by Marchand, (*J. pr. Chem.* 16, 372).

*b.* With Acids, forming the Salts of Mercuric Oxide, or Mercuric Salts.—These salts are obtained by dissolving mercuric oxide in acids, by double decomposition, and by dissolving metallic mercury in an excess of hot sulphuric or nitric acid. Mercuric salts are likewise formed, with evolution of ammonia, on boiling the oxide with various ammoniacal salts; such is the case with sulphate, hydrochlorate, nitrate, and succinate of ammonia. (Pagenstecher, *Repert.* 27, 27; Brett & L. Thompson, *Phil. Mag. J.* 10, 97, and 179; Wittstein, *Repert.* 57, 42.) Even hydrochlorate of magnesia (Berzelius), and apparently also hydrochlorate of lime, when boiled in the state of concentrated solution with mercuric oxide, give up to it a portion of their acid.

Mercuric salts, when they do not contain a coloured acid, are generally colourless in the normal, and yellow in the basic state. They are violent acrid poisons, and have a disagreeable, metallic taste. The normal salts redden litmus. Some of them are resolved by water into an acid salt, which dissolves, and a basic salt which remains behind. From their aqueous solutions, the mercury is for the most part precipitated in the metallic state, by the same substances as from mercurous salts, (p. 6), but the complete reduction of the mercury is often preceded by a conversion of the mercuric into a mercurous salt. Small quantities of phosphorous acid convert mercuric into mercurous salts; larger quantities throw down metallic mercury. (Braamcamp & Siqueira.) Sulphurous acid added to mercuric nitrate, first throws down white mercurous sulphate, which, by a larger addition of sulphurous acid, is completely converted, in the course of 24 hours, into mercury; but even when the sulphurous acid is added in excess, a portion of mercury still remains dissolved, and is not precipitated till the liquid is boiled. Terbasic mercuric sulphate dissolves in sulphurous acid, with a white turbidity, arising from the formation of mercurous sulphate, and deposits the whole of the mercury on boiling. (A. Vogel.) [For the behaviour of corrosive sublimate with sulphurous acid, see *Corrosive sublimate.*] Those metals which reduce mercury from mercurous nitrate, likewise separate it, though less quickly, from mercuric nitrate, the reduction being attended with the separation, in greater or smaller quantity, of a white or yellow powder, which, when zinc, cadmium, or copper is the reducing agent, consists of basic mercurous nitrate; in the case of bismuth, of monobasic bismuth-nitrate; and with antimony and lead, of a mixture of basic mercury-salt and basic antimony or lead-salt. Tin instantly produces black-brown clouds, which rise in the liquid, solidify in capillary tufts, assume the metallic lustre at the surface of the liquid, and ultimately form a metallic film; at the same time a small quantity of yellow basic mercuric nitrate is produced. (Fischer, *Pogg.* 9, 258.) [For the behaviour of metals with protochloride of mercury, see the latter.] If a piece of tin in contact with a gold plate be introduced into the solution of a mercuric salt acidulated with hydrochloric acid, the gold

plate becomes amalgamated, and does not lose its silver-white colouring by immersion in hydrochloric acid, though it gives it up when heated. (Smithson.) To impart a distinct white colouring to the gold by this process, the strength of the solution must not be less than 1 part of protochloride of mercury to 5000 parts of water. (Lassaigne.) A small quantity of protochloride of tin added to mercuric salts, throws down dichloride of mercury; a larger quantity of the tin-solution converts the latter into metallic mercury. Sugar boiled with mercuric acetate converts it into mercurous acetate. (A. Vogel.)

Phosphuretted hydrogen gas passed through the solution of a mercuric salt, throws down a partly white, partly yellow compound of triphosphide of mercury, with a portion of the original mercuric salt, which, moreover, is not further decomposed by an excess of phosphuretted hydrogen. (H. Rose, *Pogg.* 40, 75.)—Arseniuretted hydrogen gas produces a brown precipitate in a solution of corrosive sublimate. (H. Rose.) —Hydrosulphuric acid and alkaline hydrosulphates added in excess to mercuric salts, throw down amorphous protosulphide of mercury in black flakes. Even with 20,000 parts of water to 1 part of protochloride of mercury, sulphide of potassium produces a slight browning of the liquid, and with 40,000 parts of water, a slight greenish-brown colouring. (Lassaigne.) Absolute alcohol which has absorbed 6 measures of hydrosulphuric acid gas, does not act on dry mercuric salts. (Parnell.) The black precipitate is insoluble in hydrosulphate of ammonia or of potash. (According to Mialhé, *N. Ann. Chim. Phys.* 5, 170, it dissolves completely in these reagents.) The black sulphide of mercury is likewise insoluble in ammonia, but dissolves completely in potash—provided there is a sufficient quantity of hydrosulphate of ammonia present—and is reprecipitated by acids. (H. Rose.) When covered with aqueous hydrosulphite of ammonia or hydrosulphite of potash, it is converted, slowly in the cold, but quickly when heated, into a red powder of cinnabar.—An insufficient quantity of hydrosulphuric acid or an alkaline hydrosulphate, throws down from most mercuric salts a white compound of sulphide of mercury, with the undecomposed salt. (H. Rose, *Pogg.* 13, 59.) The precipitate is often black, brown, or yellow, from excess of sulphide of mercury, but soon turns white by taking up undecomposed salt from the liquid. It is only from the solution of the cyanide of mercury, that the pure black sulphide is thrown down by a quantity of sulphuretted hydrogen not sufficient to precipitate the whole.—Hydrochlorate or nitrate of mercuric oxide forms, with excess of hyposulphite of soda, a white precipitate, which re-dissolves in excess; with a smaller quantity of the soda-salt, the whole precipitate remains undissolved, immediately turning yellow and then brown, and is afterwards converted, slowly in cold, but quickly on boiling, into black protosulphide of mercury. If the mercuric salt is in excess, the white precipitate, which is a compound of sulphide of mercury and the salt, retains its colour. (H. Rose, *Pogg.* 33, 240.) According to Wackenroder (*Repert.* 61, 24), the precipitate is of a fine lemon-yellow colour, but becomes yellowish-white if an excess of mercuric nitrate is present; whereas, if the alkaline hyposulphite is in excess, it changes first to brown, and afterwards to black. Hydrochloric acid and sal-ammoniac impart to it a colour varying from reddish-yellow to yellowish-brown; nitric acid, from light yellow to white; and carbonate of ammonia slowly turns it black. It is not soluble in acetic acid.— Hydriodic acid and iodide of potassium added to mercuric salts, yield a scarlet precipitate of iodide of mercury. At first the precipitate exhibits

a very pale red colour. It is soluble in excess, both of the mercuric salt, and of the iodide of potassium. If the proportion of protochloride of mercury is less than 1 part to 5000 parts of water, the red precipitate does not appear. (Lassaigne.) — Hydrobromic acid and bromide of potassium, hydrochloric acid and common salt, do not precipitate mercuric salts.

Caustic ammonia and carbonate of ammonia form white precipitates with mercuric salts. This precipitate usually contains a compound of amide of mercury with undecomposed mercuric salt, and is insoluble in excess of ammonia. With 10,000 parts of water to 1 part of protochloride of mercury, ammonia produces turbidity and a precipitate; with 20,000 parts of water, a slight, and with 40.000, a scarcely perceptible opalescence. (Lassaigne, *J. Chem. méd.* 8, 582.)—Fixed alkalis in excess produce a light orange-yellow precipitate. This precipitate is not a hydrate, but consists of finely-divided anhydrous oxide. (Proust.) If the solution contains much free acid, potash gives no precipitate, or but a slight one after a considerable time. If it contains an ammoniacal salt, the precipitate produced by potash is white. When sugar, gum, and other fixed organic compounds are present in a dilute solution of a mercuric salt, potash produces, after a considerable time, a black precipitate; more concentrated solutions, under the same circumstances, yield a dirty yellow precipitate, which turns black in a few hours, or immediately on boiling, from reduction of the protoxide of mercury to dioxide.—Monocarbonate of potash or soda throws down brown-red mercuric carbonate. The presence of sal-ammoniac and of organic matters produces the same effect in this case as with the fixed alkalis.—Bicarbonate of potash added to sulphate or nitrate of mercuric oxide, immediately produces a brown-red precipitate. But with the hydrochlorate, it produces a white precipitate, which in a few minutes assumes, first a reddish, and then a deep purple-red colour. (Schindler, *Mag. Pharm.* 33, 29.) If the potash-salt does not contain fully 2 atoms of carbonic acid, the precipitate is brown-red from the beginning. (Schindler.)—The carbonates of baryta, strontia, lime, and magnesia, precipitate mercuric salts, even in the cold. (Demarçay.)—Phosphate of soda throws down from most mercuric salts (not from the chloride) a white precipitate of mercuric phosphate. The precipitation takes place down to the 500th degree of dilution. (Pfaff.)—Chromate of potash forms with mercuric solutions, not too dilute, a yellowish red precipitate.—Ferrocyanide of potassium yields, with solutions of not less than a certain strength, a white precipitate, which turns blue after long standing.—Tincture of galls gives an orange-yellow precipitate with all mercuric salts, excepting the hydrochlorate.—Aqueous cyanide of mercury does not exhibit the greater number of these reactions.

Those mercuric salts which do not dissolve in water, are nearly all soluble in hydrochloric or nitric acid; several of them likewise dissolve in hydrochlorate or nitrate of ammonia. Many mercuric salts form double salts with the salts of ammonia, potash, and soda.

*c.* With ammonia.

Mercuric nitrate in the circuit of the voltaic battery, at first deposits on the positive wire a small quantity of *peroxide of mercury*, which is subsequently converted into basic (?) nitrate of mercuric oxide. (Fischer, *Kastn. Arch.* 16, 218.)

## Mercury and Carbon.

A. Carbonate of Mercurous Oxide, or Mercurous Carbonate. —Precipitated in the form of a yellow powder, on mixing mercurous nitrate with carbonate of potash or soda. To obtain the salt completely saturated with carbonic acid, mercurous nitrate is mixed with a slight excess of bicarbonate of potash, and the mixture set aside for a few days and frequently stirred, to ensure the decomposition of any basic mercurous nitrate that may be mixed with the precipitate, which is then washed as quickly as possible, and dried in vacuo over oil of vitriol. (Setterberg, *Pogg.* 19, 53.) This preparation gives the analysis *a*. Or, crystallized mercurous nitrate is rubbed up with bicarbonate of potash and water, and the product quickly washed. (H. Rose, *Pogg.* 53, 117.)— The salt has a strong tendency to give off carbonic acid, and resolve itself into a mixture of mercuric oxide and metallic mercury. This decomposition takes place, even when the salt is left to stand under slightly warmed water (Wittstein), and immediately on boiling (H. Rose). If the salt be prepared by precipitation with monocarbonate of potash or soda, an excess of the latter blackens the precipitate by abstracting its carbonic acid. (Pfaff.) Aqueous ammonia blackens the precipitate; dissolves it, on digestion, with separation of metallic mercury; and, on subsequent exposure to the air, deposits a white powder, and leaves, on evaporation, a compound of mercuric oxide with ammonia. (Wittstein, *Repert.* 57, 42.) The salt, when exposed to the air, is converted into mercuric oxide. (Proust.)

Setterberg's analyses were made with the following preparations:— *a*. Prepared by Setterberg's method above described.—*b*. By the same method, but dried in the air instead of in a vacuum.—*c*. By dropping mercurous nitrate into bicarbonate of potash, washing, and drying in the air, whereupon the precipitate turns blackish; it is free from nitric acid. According to Lefort (*N. J. Pharm.* 8, 5), this is the only way of obtaining a product of constant composition.—*d*. By precipitating mercurous nitrate with excess of bicarbonate of potash, filtering immediately, washing, and drying. The precipitate thus obtained is not quite free from nitric acid. (Setterberg.)

| | | | Setterberg. | | | |
|---|---|---|---|---|---|---|
| | | | *a*. | *b*. | *c*. | *d*. |
| $Hg^2O$ | 208 | 90·44 | 90·79 | 91·49 | 96·59 | 92·16 |
| $CO^2$ | 22 | 9·56 | 9·21 | 7·89 | 2·89 | 7·17 |
| HO | | | | 0·62 | 0·52 | 0·67 |
| $Hg^2O,CO^2$ | 230 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

B. Carbonate of Mercuric Oxide, or Mercuric Carbonate. Monocarbonate of potash or soda gives a brown-red precipitate with mercuric nitrate. From a solution of corrosive sublimate, alkaline bicarbonates throw down, not mercuric corbonate, but oxychloride of mercury.— When the mixture of the mercuric salt with the alkaline bicarbonate is boiled, the precipitate retains scarcely a trace of carbonic acid, the less in proportion as the boiling is continued longer. (Setterberg.) The brown-red salt is slightly soluble in aqueous carbonic acid and in carbonate of potash. (Berzelius.) It dissolves in aqueous sal-ammoniac. (Wittstein, Brett.)

| | | | | | Setterberg. | | R. Phillips. |
|---|---|---|---|---|---|---|---|
| $4HgO$ | 432 | .... | 95·16 | ..... | 94·82 | ..... | 96·1 |
| $CO^2$ | 22 | .... | 4·84 | ..... | 4·78 | ..... | 4·4 |
| $HO$ | | .... | | ..... | 0·40 | ..... | |
| $4HgO,CO^2$ | 454 | .... | 100·00 | ..... | 100·00 | ..... | 100·5 |

Setterberg (*Pogg.* 19, 60) precipitated mercuric nitrate in the cold with excess of bicarbonate of potash; Phillips (*Ann. Phil.* 26, 109,) with monocarbonate.

With *Boracic acid*, neither mercurous nor mercuric oxide appears to combine.

Heated aqueous boracic acid does not dissolve mercurous oxide; neither does it precipitate mercurous nitrate: when evaporated to dryness with that salt, it may be completely dissolved out by alcohol, the mercurous nitrate remaining behind. The grey-green (or yellowish white) precipitate which borax forms with mercurous nitrate, contains no boracic acid, but consists of basic mercurous nitrate. Borate of ammonia added in small quantity to mercurous nitrate forms a black precipitate, which contains no boracic acid, but consists merely of Hahnemann's quicksilver; large quantities produce a grey precipitate, likewise free from boracic acid. (Gossmann, *Repert.* 61, 311.)—Borax neutralized with boracic acid gives with mercurous nitrate an abundant light yellow precipitate, consisting of basic nitrate, with only 1 per cent. of boracic acid adhering to it. (Anthon, *Repert.* 63, 22.)—When crystallised mercurous nitrate is triturated with borax, and the product treated with a small quantity of cold water, a dingy yellow precipitate is produced, which is blackened by a larger addition of water, and gives up a large quantity of mercuric salt to boiling water, metallic mercury with a little mercuric oxide remaining behind. (H. Rose.)

Aqueous boracic acid boiled with mercuric oxide takes up no more of it than pure water; it likewise gives no precipitate, either with the hydrochlorate or nitrate of mercuric oxide. Even when it is evaporated with mercuric nitrate till the liquid dries up and nitrous fumes begin to escape, the whole of the boracic acid may be extracted from the reddish yellow residue by alcohol. The brown-red precipitate—resembling mosaic gold, when the solution is dilute—which boracic acid forms with corrosive sublimate, contains no boracic acid, but consists of mercuric oxychloride. Similarly, the white precipitate which mercuric nitrate yields with small quantities of borax, and the aurora-red precipitate which it forms with larger quantities, consists of basic nitrate of mercuric oxide. Borate of ammonia forms, both with hydrochlorate and with nitrate of mercuric oxide, a white precipitate, free from boracic acid; the former is *white precipitate;* the latter contains mercuric oxide, nitric acid, and ammonia. (Gossmann.)—Borax neutralized with boracic acid likewise forms, with hydrochlorate of mercuric oxide, a red-brown precipitate of mercuric oxychloride, smaller, however, in quantity than that which ordinary borax produces; with nitrate of mercuric oxide, it forms a light yellow precipitate of basic nitrate, containing only 1 per cent. of boracic acid. (Anthon.)

Tünnermann (*Kastn. Arch.* 20, 23) states that he has obtained definite compounds of mercurous and mercuric oxide with boracic acid.

## Mercury and Phosphorus.

A. Phosphide of Mercury.—This compound is formed: 1. By heating *Æthiops per se* with $1\frac{1}{2}$ pt. phosphorus. (Pelletier); 2. By digesting 2 parts of mercuric oxide with $1\frac{1}{2}$ phosphorus and 1 water, mercuric phosphate being formed at the same time. (Pelletier); 3. By decomposing heated calomel with vapour of phosphorus. (H. Davy); 4. By boiling aqueous protochloride of mercury with phosphorus. (Boullay); 5. In the decomposition of aqueous mercurous nitrate by phosphuretted hydrogen gas. (Thomson); 6. When phosphuretted hydrogen gas is passed over dry, slightly heated protochloride of mercury, whereupon the phosphide of mercury sublimes. (H. Rose.)

Phosphide of mercury (1 & 2) is black; may be cut with a knife; gives off, when distilled, first the phosphorus and afterwards the mercury; and, when exposed to the air, gradually loses its phosphorus by oxidation.—That prepared by method (3) is brown (H. Davy), brown-red (Berzelius); according to Davy, it remains solid at the boiling point of mercury, and may be preserved unaltered.—That prepared by (5) has the form of dark brown flakes.—The preparation (6) is an orange-yellow sublimate, which, when somewhat suddenly heated, is resolved into phosphorus and mercury. (H. Rose, *Pogg.* 24, 335.)

B. Phosphate of Mercurous Oxide, or Mercurous Phosphate.—Diphosphate of soda added to mercurous nitrate throws down a white crystalline powder. At a red heat, the salt gives off mercury, and is converted into fused mercuric phosphate, which solidifies in a yellow glass. (Dulong, *Mém. d'Arcueil*, 3, 445.) When boiled with water, it yields a grey mixture of mercury and undecomposed salt, while the liquid takes up a large quantity of mercuric phosphate. (H. Rose.) Immersed in hydrochloric acid, it turns grey, but blackens on boiling, metallic mercury being separated, and mercuric oxide, together with phosphoric acid, dissolving. (Trommsdorff.) It dissolves imperfectly in solution of sal-ammoniac. (Brett.) The salt digested with aqueous caustic ammonia, or carbonate of ammonia, yields a filtrate containing phosphoric acid and mercuric oxide, and a residue which, besides mercurous oxide, likewise contains mercuric oxide, metallic mercury, and ammonia. (Wittstein.) Cold potash-ley decomposes the salt completely; the liquid is free from mercury; carbonate of potash decomposes it with the aid of heat, and takes up at the same time a small quantity of mercury. Aqueous sulphurous or phosphorous acid added to this salt slowly reduces the mercury. (Trommsdorff, *N. Tr.* 17, 1, 263.) The salt is insoluble in water, and likewise in aqueous phosphoric or tartaric acid.

| | | | Trommsdorff, *dried at* 100°. |
|---|---|---|---|
| $2Hg^2O$ | 416·0 | 85·35 | 85·9 |
| $PO^5$ | 71·4 | 14·65 | 14·4 |
| $2Hg^2O, PO^5$ | 487·4 | 100·00 | 100·3 |

C. Pyrophosphate of Mercurous Oxide, or Mercurous Pyrophosphate.—When crystallized mercurous nitrate is triturated with di-pyrophosphate of soda and cold water, a blackish precipitate is obtained, and the liquid takes up a mercurous salt, free from mercuric oxide. Boiling water makes the precipitate still blacker, and forms a

solution containing mercuric and mercurous phosphates. (H. Rose.) Mercurous pyrophosphate dissolves in excess of pyrophosphate of soda. (Stromeyer.) Mercurous nitrate was found by Gmelin to yield, with di-pyrophosphate of soda, a white precipitate, which neither blackened nor dissolved when treated with an excess of the soda-salt.—¶. According to Schwarzenberg, the salt obtained by precipitating mercurous nitrate with di-pyrophosphate of soda is a heavy, white, crystalline powder, soluble in nitric acid, and leaving a residue of mercuric metaphosphate when ignited. It is decomposed by hydrochloric acid. When recently precipitated, it is soluble in excess of the soda-salt; and the solution, when boiled, deposits a black powder. If the salt be dried at 100°, it is afterwards insoluble in pyrophosphate of soda, and turns black, when treated with that substance. It contains 83·45 per cent. of mercurous oxide. (Schwarzenberg, *Ann. Pharm.* 65, 159.) ¶

D. Phosphate of Mercuric Oxide, or Mercuric Phosphate.—Formed by precipitating mercuric nitrate with diphosphate of soda. Chloride of mercury is not precipitated by the soda-salt. Mercuric phosphate is a white, heavy powder, which assumes a transient yellow colour when heated. (Trommsdorff.) Bakes together when heated, and fuses into a dark yellow glass, which solidifies in a transparent mass on cooling. Heated more strongly in a glass tube, it gives off mercury, oxygen gas, and phosphorous acid [?], and leaves a residue which does not exhibit any acid reaction—is insoluble in water—still contains mercury—and evaporates completely on continued ignition. (Trommsdorff.) Aqueous ammonia extracts from the salt a small quantity of mercuric oxide, besides phosphoric acid. (Wittstein, *Repert.* 57, 60.) Caustic potash extracts all the acid, without dissolving the mercuric oxide. Carbonate of potash takes up only part of the acid, but at the same time dissolves a portion of the mercuric oxide, which does not separate from it, even on boiling. Aqueous phosphorous or sulphurous acid reduces the mercury of the salt slowly and incompletely. Cold dilute hydrochloric acid dissolves the salt slowly; the same acid, when hot and dilute, dissolves it rapidly; and the cold concentrated acid dissolves it quickly and abundantly, and with evolution of heat. From the solution in hydrochloric acid, protochloride of tin throws down mercury, together with stannic phosphate. From the residue obtained by evaporating the hydrochloric acid solution to dryness, hot alcohol extracts protochloride of mercury, which crystallizes when the alcohol is evaporated. Hence it appears that hydrochloric acid takes mercuric oxide from phosphoric acid. One part of the salt dissolves completely in the aqueous solution of 6 parts of sal-ammoniac—a small quantity of ammonia being given off, if the liquid is hot. The solution, which reddens litmus, contains hydrochlorate of mercuric oxide and ammonia, and phosphate of ammonia. (Trommsdorff, *N. Tr.* 17, 1, 263.) The salt likewise forms clear solutions with carbonate, sulphate, and nitrate of ammonia. (Wittstein.) It dissolves in aqueous phosphoric acid, but not in water or alcohol.

| | | | | | Trommsdorff, *dried at* 100°. | | Braamcamp & Siq. Oliva. |
|---|---|---|---|---|---|---|---|
| $2HgO$ | 216·0 | .... | 75·16 | .... | 75·20 | .... | 71·5 |
| $PO^5$ | 71·4 | .... | 24·84 | .... | 24·78 | .... | 28·5 |
| $2HgO, PO^5$ | 287·4 | .... | 100·00 | .... | 99·98 | .... | 100·0 |

¶. This salt appears to be really a pyrophosphate; at all events, the

mercuric pyrophosphate described by Schwarzenberg (*Ann. Pharm.* 65, 160) is identical with it in composition, and exhibits similar properties. ¶

## Mercury and Sulphur.

A. Disulphide of Mercury or Mercurous Sulphide.—Formed by dropping a solution of mercurous nitrate into aqueous bi-hydrosulphate of potash; or by pouring the latter solution on recently-precipitated and still moist dichloride of mercury; or by passing hydrosulphuric acid gas through an aqueous solution of mercurous acetate. When that gas is passed through mercurous nitrate, the nitric acid, as it is set free, decomposes the hydrosulphuric acid. The precipitate is washed with cold water, and dried over oil of vitriol at ordinary temperatures. (Berzelius.)

Black powder.—It is resolved by a gentle heat into protosulphide of mercury and metallic mercury, which may be recognized by the microscope, and unites into globules when triturated. When somewhat strongly heated, it gives off mercury, and afterwards sublimes in the form of cinnabar. (Berzelius, *Lehrb.*) Brande also (*Quart. J. of Sc.* 18, 292) regarded the precipitate produced in mercurous salts by hydrosulphuric acid and alkaline hydrosulphates, as disulphide of mercury; Guibourt, on the other hand, regarded it as a mixture of mercury and the protosulphide, because it yielded metallic mercury by pressure [had it been heated?], and was resolved by heat into mercury and cinnabar.

| | | | |
|---|---|---|---|
| 2Hg ..... | 200 | ..... | 92·59 |
| S ..... | 16 | ..... | 7·41 |
| $Hg^2S$ ..... | 216 | ..... | 100·00 |

B. Protosulphide of Mercury, or Mercuric Sulphide. — *a. Crystalline* or *Red Sulphide.*—*Cinnabar, Cinnabaris, Vermilion.*—*Formation and Preparation.*—1. *In the dry way.*—Mercury, mercuric oxide, or trisulphate of mercuric oxide, sublimed with sulphur, yields cinnabar. When 5 or 6 parts of mercury are added to 1 part of melting sulphur, and the mixture heated, with constant stirring, till the sulphur becomes thick, combination takes place suddenly, attended with evolution of light and heat, and with violent crackling and projection of the mass. The resulting compound exhibits a blackish-red colour, and frequently a distinct red streak; it may be regarded as cinnabar partly mixed with black sulphide of mercury, and partly with uncombined mercury and sulphur in a state of minute division. Now, when this crude product, after being pounded, is mixed with a small quantity of sulphur, and a glass flask half-filled with it is loosely closed with a charcoal stopper, sunk to two-thirds of its depth in sand, and exposed for some hours to a red heat in a slow-drawing wind-furnace, a sublimate of pure cinnabar is obtained. The excess of sulphur, being more volatile than the cinnabar, escapes; foreign metals remain in the form of sulphides at the bottom of the flask. If the upper part of the flask becomes too hot, a portion of the cinnabar may be lost by volatilization.

*Old method of preparation in Amsterdam.* 170 pounds of mercury are gradually added to 50 pounds of melted sulphur contained in a cast-iron pot, the materials being stirred up with an iron spatula, but not so rapidly as to give rise to active combustion—the mixture poured out upon an iron plate, and broken into pieces after cooling—and the frag-

ments put into hand-jars capable of holding 1½ pounds of water. The subliming vessels are earthen cylinders 4 feet high, glazed within, and closed at the bottom; they are sunk to two-thirds of their depth in a furnace in which their lower part is heated to redness. A few hand-jars full of the mixture are thrown into each of these subliming vessels, and the contents left to crackle and burn, till the greater part of the excess of sulphur volatilizes, and the flame diminishes. The smooth, level opening is then covered with a thick, smooth plate of cast-iron: the plate removed as soon as a sufficient quantity of cinnabar has collected upon it; the cinnabar which has collected on the upper part of the vessel pushed down again; a fresh plate put on, &c. &c. The contents of the cylinder are stirred up from time to time, and fresh material introduced. The cinnabar, after being detached from the plates, is ground as finely as possible with rain-water.

*Method of preparation in Idria.* A number of casks, each containing 8 pounds of pounded sulphur and 42 pounds of mercury, are made to turn upon their axes for two or three hours, till the contents are converted, with slight evolution of heat, into a brown powder. 100 pounds of this powder are then introduced into an upright cast-iron cylinder, previously heated in a furnace; the cylinder covered with an iron capital, kept down by weights, till the crackling of the mass is over; the iron capital thereupon replaced by one of stone-ware, having its beak connected with a tube and receiver, and the fire increased. The best cinnabar collects in the capital, which is afterwards broken in pieces; that which condenses in the tube and receiver, if mixed with excess of sulphur, is added to the quantity introduced at the next sublimation. The cinnabar, after being finely ground with water, is well boiled with potash-ley, and washed with boiling and with cold water. (Mitscherlich, *Lehrb.*)

*Chinese method.* 1 part of sulphur and 4 parts of mercury are sublimed in an earthen vessel, to which an iron cover, kept constantly moist, is luted; the fire is kept up for four-and-twenty hours; the vessel broken up after cooling; the less pure sublimate separated; the purer portion pounded up, and the powder sifted into a large vessel filled with water; the water, with the scum floating on it, poured off after a while, the process being twice repeated; and lastly, the sediment at the bottom is dried. (*N. Edinb. J. of Sc.* 2, 352.)

European cinnabar, whether prepared in the dry or in the humid way, always has a tinge of yellow; the Chinese, which is six times as dear, inclines to carmine colour, although no foreign matter can be detected in it, excepting a little glue. By the sublimation of common cinnabar with 1 per cent. of sulphide of antimony, a dark steel-grey cinnabar is obtained, which becomes brown-red when pulverized: but if it be finely ground, and repeatedly boiled with solution of liver of sulphur, then thoroughly washed and digested with hydrochloric acid, and afterwards washed and dried, it becomes exactly like the Chinese vermilion, but of a still finer colour. No antimony can be detected in it. (Wehrle, *Zeitschr. Phys. v. Wiss.* 2, 27.)

The principal point to be attended to in the preparation of cinnabar by sublimation, is that no black, amorphous sulphide get mixed with it.

2. *In the humid way.* The black, amorphous sulphide of mercury obtained by the action of hydrosulphuric acid, or of alkaline hydrosulphates or hydrosulphites on mercury, its oxides, and salts, is converted by contact with alkaline hydrosulphites, slowly in the cold, but quickly when heated, into the red sulphide.

Mercury, agitated and digested with Boyle's spirit of sulphur (II. 454) yields cinnabar. (Fr. Hoffman, *Observ. phys. chem. Lib.* 2, *Obs.* 31.) Mercury agitated with Boyle's spirit of sulphur is immediately converted into a black powder, which, after three days' immersion in the liquid, is converted into fine spiculæ of crystallized cinnabar. A similar result is obtained with pulverized sulphide of mercury, obtained by fusing sulphur and mercury together with mercuric oxide, and likewise with the trisulphate and monosulphate of mercuric oxide, excepting that the latter become heated by contact with the spirit of sulphur, and require a larger quantity of it to convert them into cinnabar. The black precipitate, also, which spirit of sulphur yields with mercurous nitrate, acquires a splendid red colour after a few hours' immersion in fresh spirit of sulphur. The black precipitate obtained from protochloride of mercury does not change into cinnabar in less than a year. Potassic liver of sulphur acts much more slowly than Beguin's spirit. (Baumé, *Chim. experiment.* 2, 466.) The black precipitate which the sulphates, hydrochlorates, and nitrates of mercury yield with ammoniacal or potassic liver of sulphur, turns red slowly and after long standing, at ordinary temperatures, but rapidly when heated. Protochloride of mercury yields remarkably fine cinnabar. Ammoniacal liver of sulphur yields a more finely-coloured product than potassic liver of sulphur. (Proust, *Gilb.* 25, 174.)

The black powder obtained by triturating 7 parts of mercury with 2 parts of sulphur till the fluidity of the metal is destroyed, acquires a red colour when immersed in a solution of potassic liver of sulphur at 45°, and yields 7·05 parts of moderately good cinnabar. The black powder likewise yields cinnabar when immersed in sodic liver of sulphur and hydrosulphate of ammonia, but not in caustic ammonia. Mercuric oxide blackens when immersed in hydrosulphate of ammonia, but afterwards turns gradually red from top to bottom, and after 14 days yields 106·2 per cent. of bright red cinnabar, which sublimes without residue. With potassic liver of sulphur, the product obtained consists of 101·65 per cent. of cinnabar, which has a yellowish iridescence, and when sublimed yields a small quantity of metallic mercury as well as cinnabar. Calomel digested with hydrosulphate of ammonia, blackens at first, and after several days yields 96·7 per cent. of brown-red cinnabar; with potassic liver of sulphur, it yields 99·5 per cent. Trisulphate of mercuric oxide digested for 8 days in hydrosulphate of ammonia, yields 94·17 per cent. of crystals, having the dark colour of sublimed cinnabar, and becoming bright red by trituration; a small quantity of mercury is found in the liquid. In solution of potassic liver of sulphur, the mercuric sulphate yields 102·9 per cent. of dingy yellowish-red cinnabar, which sublimes without residue, and is thereby converted into ordinary cinnabar; the liquid contains no metallic mercury. *Mercurius solubilis* immersed for a few days in hydrosulphate of ammonia, yields 99·9 per cent. of a violet-red crystalline powder, consisting of cinnabar, which sublimes without residue; with potassic liver of sulphur, it yields 101·2 per cent. of brown-red, pulverulent cinnabar. (Brunner, *Pogg.* 15, 600,) When recently prepared white precipitate is immersed in bi-hydrosulphate of ammonia, or in monosulphide of ammonium previously saturated with sulphur, the black colour which it first acquires, passes at 40° or 50°, through red-brown into the beautiful dark carmine-red of Chinese vermilion, the change taking place more quickly as the liquid is more concentrated. The colour may be rendered still brighter by subsequent digestion with strong potash at a gentle heat. (Liebig, *Ann. Pharm.* 5, 289; 7, 49.)

The black precipitate which hydrosulphuric acid or hydrosulphate of ammonia yields with mercuric salts, is converted by immersion in alkaline hydrosulphates into cinnabar, the change taking place the more easily as the temperature is higher, and as the alkaline hydrosulphate contains a larger excess of sulphur. (Gm.) The red colouring of the black sulphide of mercury, produced by treating it with solution of liver of sulphur, is due to crystallization, which is rendered possible by its solubility in the liver of sulphur.

*Particular modes of preparation in the humid way:*

Kirchhoff (*Scher. J.* 2, 290) triturates in a porcelain dish, 100 parts of mercury with 23 parts of flowers of sulphur, moistening the mixture with potash-ley, till the fluidity of the mercury is destroyed; he then warms the mass, still triturating constantly, in a solution of 53 parts potash-hydrate in 53 parts water, replacing the water as it evaporates, till, in about two hours, the black colour of the mixture changes to brown, and then quickly to red. The mass is then evaporated, still with constant trituration, to a thin paste, till the red colour has attained its utmost degree of brightness, whereupon the heat is immediately removed. If the heat be not continued long enough, the fine red colour is not fully developed; and if it be applied only a few seconds too long, the colour changes to brown, and cannot be brought back again to red. (Kirchhoff.) In consequence of the too great excess of potash, a portion of the sulphide of mercury dissolves in the liver of sulphur, and is deposited on the addition of water. In this process, therefore, it is necessary to wash, first with potash, and then, but not before, with water. (Brunner.)

Bucholz (*Scher. J.* 9, 170; also *Crell, Ann.* 1802, 1, 27) heats and agitates for 4 hours, and then digests for 12 hours, a mixture of 4 parts of mercury, 1 of sulphur, 3 of potash-hydrate, and 6 of water.

Brunner (*Pogg.* 15, 593) carefully triturates 100 parts of mercury with 38 parts of flowers of sulphur, till the whole is converted into Æthiops—a process which requires 3 hours for small quantities, and 12 hours if the quantity amounts to a few pounds—and heats it in a porcelain basin or a cast-iron pot, with a solution of 25 parts of potash-hydrate in 133 to 150 parts of water, keeping the temperature uniformly at 45°, and never letting it rise above 50°. At first, the mixture is continually stirred with the pestle, afterwards from time to time. The water which evaporates is replaced, so as not to allow the mixture to acquire the thickness of a jelly. When the reddening has once begun, which generally takes place in about 8 hours, the heat must not be allowed to rise above 45°; and as soon as the red has attained its greatest degree of brightness, the vessel is removed from the fire, or else, which is better, the mixture is kept for some hours exposed to a gentler heat. It is then washed, and the mercury which remains metallic, separated by levigation, whereupon it yields from 109 to 110 per cent. of cinnabar, but little inferior to the finest native variety, and far superior to that obtained by sublimation. The above-mentioned proportion of the ingredients gives the largest amount of cinnabar. 100 parts of mercury yield with 40 parts of sulphur and 40 of potash-hydrate, 107 cinnabar; with 28·3 sulphur and 51 potash-hydrate, 94·2; with 33 to 40 sulphur and 60 potash-hydrate, 81·5; and with 30 sulphur and 60 potash-hydrate, only 47·3 cinnabar. (Brunner.

Döbereiner (*Schw.* 61, 380) gently heats mercury with a solution of pentasulphide of potassium, triturating it continually, till the mercury is converted into a dark red powder, a change which generally takes place in about an hour and a half; he then decants the liquid (which contains

protosulphide of potassium, and by digestion with sulphur may be rendered fit for another preparation of cinnabar), and triturates the powder with a small quantity of dilute potash-ley at 40° or 45°, till it acquires a fiery red colour.

If the cinnabar has become brown from being heated too long with sulphur and potash-ley, it may be restored to the state of the finest vermilion by the addition of water and the application of a moderate heat. (Storch, *Repert.* 35, 107.)

Th. Martius (*Kastn. Arch.* 10, 497) places the ingredients in bottles closed with corks, and packs them in a box, which is fastened to the upper beam of a saw-mill. In 24 or 36 hours, at ordinary temperatures, the most beautiful cinnabar is obtained; it is afterwards washed and dried. This method not only has the advantage of dispensing with the labour of trituration, but it likewise prevents the hitherto unexplained passage of the cinnabar into the brown state, which is so liable to take place on the application of heat. The author is indebted to Martius for two splendid specimens of this cinnabar.

*Adulterations.*—*Brick-dust* remains behind on ignition.—*Oxide of iron* the same; it may also be dissolved out by hydrochloric acid.—*Red lead* remains behind on ignition, in the form of a fused protoxide, and yields chloride of lead, with evolution of chlorine on boiling the substance with hydrochloric acid; it may also be extracted by large quantities of boiling water.—*Dragon's Blood.* Empyreumatic odour on the application of heat; gives a red colour to alcohol.

*Properties.*—Native cinnabar and many of the artificial varieties form crystals belonging to the rhombohedral system, the primary form being an acute rhombohedron. *Fig.* 151, 135, 160, and other forms, $r^3 : r^5 = 71° 48'$; $r^1 : r^3$ or $r^5 = 108° 12'$. Cleavage parallel to *r* and *s*. Cinnabar obtained by sublimation assumes the form of fibrous masses. Specific gravity of the native mineral, 8·0 to 8·1; of the artificially sublimed compound, 8·0602 (Karsten), 8·124 (Pol. Boullay). In the mass it is cochineal-coloured, transparent, and has an adamantine lustre; its powder is scarlet. Becomes brownish when gently heated; quite brown at 250°, and black at a higher temperature; but if the heat has not been strong enough to cause it to volatilize, it recovers its fine scarlet colour on cooling.

| | | | Proust. | Guibourt. | Erdmann & Marchand. | Sefström. | Seguin. |
|---|---|---|---|---|---|---|---|
| Hg | 100 | 86·21 | 85 | 86·21 | 86·211 | 86·29 | 86·6 |
| S | 16 | 13·79 | 15 | 13·79 | 13·789 | 13·71 | 13·4 |
| HgS | 116 | 100·00 | 100 | 100·00 | 100·000 | 100·00 | 100·0 |

| | Vol. | Sp. gr. | Vol. | Sp. gr. |
|---|---|---|---|---|
| Vapour of Mercury | 6 | 41·5800 | $\frac{2}{3}$ | 4·6200 |
| Vapour of Sulphur | 1 | 6·6556 | $\frac{1}{9}$ | 0·7395 |
| Vapour of Cinnabar | 9 | 48·2356 | 1 | 5·3595 |

The opinion of Fourcroy that cinnabar likewise contains oxygen, has been refuted by Proust (*Gilb.* 25, 171) and Seguin (*Ann. Chim.* 90, 252).

¶ Bealey (*Chem. Soc. Qu. J.* IV, 180) has examined several specimens of native cinnabar: (*a*), from New Almaden, in California; (*b*), from Almaden, in Spain; (*c*), from Moschellandsberg; (*d*), from Wolfstein. The following are the mean results of the analyses:—

| | California. | | Spain. | | Moschellandsberg. | | Wolfstein. |
|---|---|---|---|---|---|---|---|
| Hg ..... | 69·90 | ..... | 37·79 | ..... | 66·86 | ..... | 18·00 |
| S ..... | 11·29 | ..... | 16·22 | ..... | 11·43 | | |
| Fe ..... | 1·23 | ..... | 10·36 | Insol. residue | 17·09 | ..... | 73·31 |
| CaO ..... | 1·40 | | | | | | |
| $Al^2O^3$ ..... | 0·61 | | | | | | |
| MgO ..... | 0·49 | | | | | | |
| $SiO^2$ ..... | 14·41 | Silica and alumina | 35·12 | | | | |
| | 99·33 | | 99·49 | | | | |

The Californian ore has a bright red colour, slightly inclining to purple, and appears to have been imperfectly cleared from a soft, light-brown earth, which can be easily scraped from its surface. It breaks without much difficulty under the hammer, and is afterwards easily reduced to powder, with the exception of some bright crystalline particles, which are extremely hard. The surfaces of recently broken ore appear much more purple than those long exposed. It is traversed at irregular intervals by very thin bands of white, hard, crystalline mineral, apparently calcareous and siliceous. In the state of fine powder, it has a very brilliant vermilion colour, much darker than that of the massive ore. Its specific gravity is 4·410. It is found in nests in a stratum of yellowish earth 42 feet thick. The vein is very large, and crops out on the surface, where it is worked. It yields a large quantity of mercury, 10,000 lbs. of which have been obtained from it in three months. The occurrence of this mineral has been known to the natives from time immemorial, as the cave of red earth, which they employed for painting their bodies. The ore from Almaden in Spain is, like the Californian ore, massive, but much less brilliant, and much harder. Throughout its mass, small yellow patches of iron pyrites are irregularly distributed. In the state of fine powder, it has a dull, brick-red colour. Sp. gr. 3·622. The ore from Moschellandsberg is dark red brown, crystalline, heavy, very hard, and difficult to pulverize. Sp. gr. 4·735. The ore from Wolfstein is a grey, earthy-looking mineral, with dark, livid patches occurring at intervals in its substance. It is very hard, and yields a light puce-coloured powder. ¶

*Decompositions.*—Cinnabar heated in the air burns with a blue flame, yielding sulphurous acid and metallic mercury. When sublimed with lamp-black or charcoal, the greater part decomposes, metallic mercury being separated, and a large quantity of hydrogen gas containing sulphur evolved. (F. C. Vogel, *Klapr. & Wolff's Worterbuch*, 5, 761.) That which Vogel took for hydrogen gas containing sulphur is really vapour of sulphide of carbon; a great part of the cinnabar remains undecomposed. (Berthier.) Cinnabar volatilized at the beginning of a red-hot tube through which a current of hydrogen is passed, yields a large quantity of hydrosulphuric acid gas, and a black sublimate containing a large number of mercurial globules, but no mercuric oxide. (Regnault.) [What becomes of the oxygen of the water?] Boiling water, aqueous alkalis, and hydrochloric acid, exert no decomposing action. Boiling oil of vitriol gives off sulphurous acid, and leaves mercuric sulphate. (Brande.) Nitric acid exerts but a feeble action, even when aided by heat. Aqua-regia acts violently, even at ordinary temperatures, dissolving the mercury in the form of mercuric oxide; while the sulphur is partly separated in the free state, and partly converted into sulphuric acid. In chlorine gas cinnabar

burns vividly, forming chloride of sulphur and chloride of mercury. Cinnabar heated with dry protochloride of tin gives off hydrochloric acid, with a trace of sulphurous acid, and leaves mosaic gold. (A. Vogel.) [In this reaction, dichloride of mercury must be evolved: $2HgS + SnCl = Hg^2Cl + SnS^2$.] Cinnabar boiled with aqueous protochloride of tin, gives off hydrosulphuric and hydrochloric acid, and is converted into a brown mixture of undecomposed cinnabar, metallic mercury, protochloride of tin, and bi-oxide of tin. (A. Vogel, *Kastn. Arch.* 23, 82.) It is difficult to understand by what reaction these products are formed. ¶. According to Bolley (*Ann. Pharm.* 75, 239), cinnabar turns instantly black when immersed in a solution of silver-nitrate containing excess of ammonia, and may be recognized with certainty by means of this reaction, even when mixed with other bodies, and used as a pigment; the reaction consists in the formation of sulphide of silver and compounds of basic nitrate of mercuric oxide with mercuric amide. According to Liebig and Kopp (*Jahresbericht*, 1850, 332), orpiment and sulphide of tin, when freshly precipitated, give the same reaction with silver-nitrate without ammonia. ¶ Iron, tin, antimony, and several other metals, withdraw the sulphur, on the application of heat, and allow the mercury to distil over. Fixed caustic alkalis and their carbonates liberate the mercury on ignition, while a mixture of metallic sulphide and alkaline sulphate remains behind:

$$4HgS + 4CaO = 4Hg + 3CaS + CaO,SO^3.$$

Carbonate of soda, and also lime, if it be mixed with a certain quantity of charcoal, produces complete decomposition of the cinnabar. (Berthier, *Ann. Chim. Phys.* 33, 161.) Cinnabar ignited with protoxide of lead gives off sulphurous acid and mercury, leaving very pure metallic lead and a fused slag, which, if the lead-oxide is not in very great excess, contains undecomposed cinnabar. 117 pts. (1 At.) of cinnabar heated in a distillatory apparatus with different quantities of litharge, yield the following results. With 446 pts. (4 At.) litharge: sulphurous acid gas, 100 pts. (nearly 1 At.) lead, and an opaque, blackish grey slag. The one atom of sulphur in the cinnabar should take up 2 atoms of oxygen from the litharge, and reduce 2 atoms of lead; but since only half that quantity of lead is really obtained, it follows that half the cinnabar must have entered without decomposition into the slag. If only a gentle heat be applied in the beginning of the action, nothing but mercury, with a small quantity of sulphurous acid, passes over; but on subsequently raising the heat to bright redness, a large quantity of sulphurous acid goes off, lead is reduced, and the above-mentioned slag is formed. With 669 pts. (6 At.) litharge: 110 parts of lead, together with a transparent, black-brown glass. With 894 pts. (8 At.) litharge: 180 parts of lead, together with a transparent, hyacinth-red glass. With 1788 pts. (16 At.) litharge: 206 pts. (nearly 2 At.) lead, together with a crystalline slag, having the appearance of litharge. For the complete desulphuration of the cinnabar, 10 atoms of litharge are probably sufficient. (Berthier, *Ann. Chim. Phys.* 39, 247.)

*b. Amorphous* or *Black Sulphide of Mercury.—Formation.* 1. Cinnabar moderately heated out of contact of air, is converted into black sulphide of mercury; at a stronger heat, however, it is reconverted into [sublimed?] cinnabar. (Seguin, *Ann. Chim.* 90, 268.) To render the black colour permanent after cooling, the cinnabar must be heated till it begins to volatilize. (Fickentscher, *Repert.* 33, 429.) As soon as the finely pounded cinnabar begins to sublime, the glass tube containing it

must be immediately plunged into cold water; the cinnabar is thereby in most cases completely converted into the black sulphide, especially if it has been prepared in the humid way. (Fuchs, *Pogg.* 31, 581.)—2. Hydrosulphuric acid and alkaline hydrosulphates added to mercuric salts, throw down black sulphide of mercury. *Pulvis hypnoticus s. narcoticus Krielii*, obtained by precipitating mercurous nitrate with potassic liver of sulphur, is black sulphide of mercury, sometimes mixed with excess of sulphur.—3. Metallic mercury agitated with excess of aqueous pentasulphide of ammonium or potassium, withdraws sulphur from that compound, and forms black sulphide of mercury. If powdered sulphur be added to the liquid, the sulphur dissolves in the protosulphide of ammonium or potassium, and reconverts it into pentasulphide, which again gives up sulphur to the remaining portion of metallic mercury, till the latter is fully saturated with sulphur. This reaction is the basis of the preparation of cinnabar in the humid way.—4. If 16 parts of sulphur be continuously triturated, at ordinary temperatures, with 100 parts of mercury, heat is evolved and the same black compound formed. When 1 part of sulphur is triturated with 8 parts of mercury, till the latter is completely deadened, the whole of the sulphur is found to be converted into sulphide of mercury (mixed with excess of mercury); for boiling potash is not coloured by contact with it; the excess of mercury may be dissolved out by dilute nitric acid. With 1 part of sulphur to 5 parts of mercury, the whole of the metallic mercury disappears after 8½ hours' trituration; and when the proportion is 1 pt. of sulphur to 3 of mercury, the whole of the metal disappears in 5 hours. (Munck af. Rosenschöld; *Pogg.* 34, 453.)

*Æthiops mineralis, Mineral black*, or *Quicksilver black*, obtained by triturating together, at the ordinary temperature, equal parts of mercury and sulphur, till the mercury completely loses its fluidity, is a mixture of black sulphide of mercury with excess of sulphur. Unless the trituration is continued for a very long time after the globules of mercury have disappeared, the mixture will still contain finely divided mercury, which may be recognized by its power of amalgamating gold, on trituration, and by its solubility in cold dilute nitric acid. When equal parts of mercury and sulphur are rubbed together till nitric acid no longer dissolves out mercury from the mixture, the excess of sulphur may be extracted by sulphide of carbon, and then a black residue is left, having the composition of cinnabar. (C. G. Mitscherlich, *Pogg.* 16, 353.)

To save the trouble of trituration, the mixture may be agitated by means of the saw-mill (as described on page 23); but to obtain a soft, black preparation, it is necessary to add a little water. If dry materials are used, a black-brown granular powder is obtained, which, though it becomes blacker by trituration, always remains lighter than the former. (Th. Martius.)

The following methods are also recommended to accelerate the deadening of the mercury.—1. To warm the mortar. (Lichtenberg.) If, however, the heat be very strong, a small quantity of cinnabar may likewise be formed.—2. To triturate a hot mixture of 1 pt. mercury, 1 pt. sulphur, and 1 pt. sugar, with a small quantity of water, replacing the water as it evaporates, and washing out the sugar after the mercury has completely lost its fluidity. (Monheim, *Repert.* 45, 273.)—3. To triturate 1 part of mercury with 1 part of sulphur, with the addition of ¼ pt. aqueous hydrosulphate of ammonia (Geiger) or hydrosulphate of potash, which is afterwards to be removed by washing. (Destouches.)

This process may likewise produce a portion of cinnabar, which has no medicinal action.—When the black sulphide is prepared by fusing mercury and sulphur together, the proportion of its constituents is indeterminate on account of the volatilization of the sulphur; and it contains a large quantity of cinnabar, which remains undissolved on boiling with potash, whereas good æthiops is either wholly or almost wholly soluble in that liquid.

Black sulphide of mercury is converted into the red sulphide, both by sublimation and by the action of aqueous alkaline hydrosulphites. Its reactions, so far as they known, are the same as those of the red sulphide, but are produced with greater facility; thus it is dissolved by hot nitric acid, with separation of sulphur.

*Alkaline Hyposulphites* form with mercuric salts, a white or yellow precipitate, which, according to H. Rose, is a compound of sulphide of mercury with the original mercuric salt (p. 13).

¶ *Pentathionic* and *Tetrathionic Acid* yield with mercurous nitrate, a yellow precipitate which slowly blackens on boiling; and with the protochloride of mercury, a yellowish precipitate consisting of a compound of sulphide and chloride of mercury mixed with free sulphur; with the cyanide, these acids gradually form a yellow precipitate, which blackens slowly in the cold, immediately on boiling. (Kessler.) ¶

*Trithionic Acid* forms with mercurous nitrate a yellowish precipitate, which turns black on adding an excess of the acid. (Fordos & Gélis.) ¶ With mercuric nitrate (Fordos & Gélis) and protochloride of mercury, it forms a white precipitate, which is a compound of sulphide of mercury and the original salt mixed with free sulphur; and with cyanide of mercury, a yellow precipitate which blackens slowly in the cold, readily on boiling. (Kessler.) ¶

C. Hyposulphate of Mercurous Oxide, or Mercurous Hyposulphate.—A solution of recently-precipitated mercurous oxide in the aqueous acid, yields indistinct colourless crystals on evaporation. These, when heated, give off mercury, mercurous sulphate, and free sulphuric acid; potash separates mercurous oxide from them. Cold water dissolves them sparingly, and hot water turns them black. Nitric acid dissolves them readily. (Rammelsberg, *Pogg.* 59, 472.)

| | *Crystallized.* | | Rammelsberg. |
|---|---|---|---|
| $Hg^2O$ | 208 | 74·29 | 74·28 |
| $S^2O^5$ | 72 | 25·71 | |
| $Hg^2O,S^2O^5$ | 280 | 100·00 | |

D. *Mercuric Hyposulphate ?*—When mercuric oxide is digested with aqueous hyposulphuric acid, and the filtrate evaporated, mercurous sulphate crystallizes out, and sulphuric acid remains in solution :—

$$2HgO + S^2O^5 = Hg^2O,SO^3 + SO^5.$$

If an excess of mercuric oxide is used in the digestion, a yellowish white powder remains on the filter, probably consisting of basic hyposulphate of mercuric oxide. When heated, it is decomposed with a hissing noise, and is partly converted into mercury and mercurous sulphate. Potash separates from it 80·84 per cent. of mercuric oxide. Hydrochloric acid dissolves it with facility. (Rammelsberg.)

E. Sulphate of Mercurous Oxide, or Mercurous Sulphate.—1. One part of mercury is gently heated with from ½ to 1 part of oil of vitriol, till somewhat more than the half of it is converted into a solid salt; the product is then freed from excess of mercury and oil of vitriol by decantation and washing with a small quantity of cold water. If the the salt be heated to dryness, the resulting mass is a mixture of mercurous and mercuric salt; and if 2 parts of mercury have been used with 1 part of oil of vitriol, it still contains a large quantity of free mercury; the mercurous salt is gradually converted by the hot oil of vitriol into mercuric salt.—2. When 18 parts of monosulphate of mercuric oxide are triturated with 6 parts of water and 11 parts of mercury, heat is evolved and the mercury is taken up. (Planche, *Ann. Chim.* 66, 168.)—3. An aqueous solution of mercurous nitrate is precipitated with sulphuric acid or sulphate of soda, and the precipitate washed with a small quantity of water. H. Rose triturates crystallized mercurous nitrate with sulphate of soda, and dissolves out the nitrate of soda with cold water.

White heavy crystalline powder, or small prisms. Fuses at a low red heat, and immediately gives off a mixture of 103 measures of sulphurous acid gas and 97 measures of oxygen, while mercury with a small quantity of sulphate, and a very small quantity of undecomposed sulphuric acid, distils over. (Gay-Lussac, *N. Gehl.* 4, 469.) By continued boiling with a large quantity of water, the salt is resolved into acid mercurous sulphate, which dissolves, and a dingy yellow powder, consisting of a mixture of metallic mercury and terbasic mercuric sulphate. (H. Rose.) Proust and Donovan regarded this yellow powder as a basic sulphate of mercurous oxide. According to Kane (*Ann. Chim. Phys.* 72, 273), no basic salt is obtained by treating this compound either with cold or with boiling water. The salt dissolves in dilute nitric acid, and is almost wholly precipitated therefrom by dilute sulphuric acid. (Wackenroder, *Ann. Pharm.* 41, 319.) It dissolves abundantly in hot oil of vitriol, from which it is partly separated in the crystalline form on cooling; another portion is precipitated by water.

| | | | | Kane. |
|---|---|---|---|---|
| $2Hg$ | 200 | 80·65 | | 80·80 |
| $O$ | 8 | 3·22 | | 3·18 |
| $SO^3$ | 40 | 16·13 | | 16·02 |
| $Hg^2O,SO^3$ | 248 | 100·00 | | 100·00 |

The salt examined by Kane was obtained by double decomposition according to (3); it appeared to be anhydrous.

F. Sulphate of Mercuric Oxide, or Mercuric Sulphate.—*a. Terbasic.—Mineral Turbite, Turpethum minerale.*.—1. The monobasic salt in the state of powder is triturated with considerable quantities of water —most advantageously with boiling water—which removes the greater part of the acid, in combination with a small quantity of oxide. If the action of the water be not continued long enough, a portion of the monosulphate remains undecomposed.—2. Mercuric nitrate is precipitated at a high temperature by sulphate of soda. When 108 parts of mercuric oxide are dissolved in nitric acid, and the solution diluted with water, mixed with sulphate of soda, and then warmed, a precipitate is formed amounting to 97·2 parts. (Geiseler.) By heating 108 parts of mercuric oxide with 16·2 parts of oil of vitriol and 540 of water, an orange-yellow mass is obtained, but not the true *turpethum*. (Geiseler.) Bright lemon-

yellow powder, assuming a reddish colour while hot. Sp. gr. 6·444. (Wattson.) Chlorine gas at ordinary temperatures decomposes it very slowly, and in the same manner as the oxide. (Pelouze.) Gives up all its acid to caustic potash. (Donovan.) Dissolves in 2000 parts of cold, and 600 of boiling water. (Fourcroy, *Ann. Chim.* 10, 307.)

| | | | Kane (1). | R. Phillips (1) |
|---|---|---|---|---|
| 3HgO | 324 | 89·01 | 88·90 | 87·4 |
| $SO^3$ | 40 | 10·99 | 10·95 | 12·6 |
| $3HgO,SO^3$ | 364 | 100·00 | 99·85 | 100·0 |

| Geiseler. | Braamcamp & Siq. Ol. |
|---|---|
| 88·41 | 87·7 |
| 11·34 | 12·0 |
| 99·75 | 99·7 |

*b. Monobasic.*—1. When 1 part of mercury is heated with $1\frac{1}{2}$ part of oil of vitriol, till the mixture is perfectly dry, sulphurous acid gas is evolved (*Sch.* 23), and a white solid mass is evolved. If only 98 parts of oil of vitriol are used to 100 of mercury (as the formula would indicate), the product is mixed with unaltered mercury [and mercurous sulphate]; when 100 parts of mercury and 125 of oil of vitriol are used, mercury sublimes after the sulphurous acid has gone off, and the residue amounts to only 128 parts instead of 148, as it ought to be. [It likewise contains mercurous salts.] 100 parts of mercury and 166 of oil of vitriol yield a residue amounting to 152 parts [the excess probably consisting of admixed oil of vitriol]. (Geiseler, *N. Br. Arch.* 14, 115.) A large quantity of undecomposed oil of vitriol evaporates with the sulphurous acid. Pure mercuric sulphate dissolves completely in concentrated hydrochloric acid; if mercurous salt is mixed with it, a white residue is left, which, after washing with water, is blackened by potash.—2. 108 parts of mercuric oxide are heated to dryness with water and more than 49 parts of oil of vitriol. 108 parts of mercuric oxide triturated with 48·6 parts of oil of vitriol form, with evolution of heat, a dry compact lump, white on the outside, yellow and red within. When heated after trituration, it yields a reddish-white powder; and if this powder is heated with excess of oil of vitriol, till the latter evaporates, there remain 151·2 parts of salt. 108 parts of mercuric oxide heated with 540 parts of water and 194·4 parts of oil of vitriol, dissolve completely, and leave, after sufficient heating, 149 parts of salt. (Geiseler.)

White opaque mass; when ignited, it first turns yellow and then red, but loses its colour on cooling. (Mohr.) At a strong red heat, it is resolved into sulphurous acid, mercury, and mercurous sulphate. A sublimate of metallic mercury is formed at the top of the tube; below that, white mercurous sulphate, and lowest of all, next to the undecomposed salt, a sublimate of mercuric sulphate. (Mohr.) The salt, when heated with charcoal, yields reduced mercury, and gives off equal measures of carbonic and sulphurous acid gases. (Gay-Lussac, *J. pr. Chem.* 11, 70.)

$$HgO,SO^3 + C = Hg + SO^2 + CO^2.$$

When triturated with aqueous hydriodic acid, it immediately yields protiodide of mercury and free sulphuric acid. (Mohr.) Mercuric sulphate and common salt decompose each other, both in the wet and in the dry way (Mialhe), yielding sulphate of soda and protochloride of mercury.

It does not absorb hydrochloric acid gas at ordinary temperatures, but when gently heated, it takes up that gas abundantly—the absorption producing a rise of temperature, by which a portion of the chloride of mercury may be sublimed—and is converted into a mixture of protochloride of mercury and oil of vitriol:

$$HgO,SO^3 + HCl = HgCl + HO,SO^3.$$

The mass does not smell of hydrochloric acid; it hisses when moistened with water, and absorbs water from the air, so that the sulphuric acid may be afterwards poured off from it in the dilute state; after the extraction of the sulphuric acid by a small quantity of cold water, there remains a residue of corrosive sublimate. After the sublimation of the mass, there remains a small quantity of mercuric sulphate, reproduced by the action of the oil of vitriol on the corrosive sublimate. (Mohr.) According to Kane (*Ann. Pharm.* 19, 5), the dry salt absorbs $\frac{1}{2}$ At. hydrochloric acid gas, the absorption being attended with rise of temperature, but not with decomposition. The hydrochloric acid thus taken up escapes rapidly on the application of heat, and slowly when the salt is exposed to the air; water extracts it immediately. Aqueous hydrochloric acid likewise acts upon dry mercuric sulphate, protochloride of mercury being produced, with great rise of temperature and evolution of sulphuric acid. (Mohr.) The vapour of anhydrous hydrocyanic acid acts only upon the heated salt, which it converts into cyanide of mercury and sulphuric acid; by too high a temperature, however, mercury is immediately reduced and mercurous sulphate formed. Aqueous hydrocyanic acid likewise acts on the salt, causing rise of temperature, and forming a solution of cyanide of mercury and sulphuric acid, or acid mercuric sulphate. The solution, when boiled, evolves gas, and deposits mercurous sulphate in the form of a white powder, while mercuric sulphate remains in solution. (Mohr, *Ann. Pharm.* 31, 180.) By water, the monobasic salt is resolved into the terbasic sulphate and a solution of the acid salt. 100 parts of monobasic mercuric sulphate treated with a large quantity of cold water, yield 70·55 parts of terbasic sulphate, and 4·2 parts more on boiling, making in all 74·75 parts; with a smaller quantity of water, 77·5 parts of the terbasic salt are obtained. By long boiling with water, 71·09 parts of terbasic salt are produced, and a solution containing 10·11 parts of mercuric oxide to 19·08 sulphuric acid [about 1 At. mercuric oxide to 5 At. acid]. R. Phillips. (*Phil. Mag. Ann.* 10, 206.) Geiseler, by boiling the monobasic salt, obtained only 68 per cent. of terbasic sulphate.

| | | | | | Kane. |
|---|---|---|---|---|---|
| $HgO$ | 108 | .... | 72.97 | .... | 72·98 |
| $SO^3$ | 40 | .... | 27·03 | .... | 27·02 |
| $HgO,SO^3$ | 148 | .... | 100·00 | .... | 100·00 |

*c. Acid Salt.*—108 pts. [1 At.] of mercuric oxide heated with water require 195 pts. [4 At.] oil of vitriol to dissolve them completely. (Geiseler.) According to the above-mentioned experiment of Phillips, 5 atoms of dilute sulphuric acid are required for 1 At. oxide. The solution when evaporated, yields crystals, which have not been further examined.

¶. F. Mercuroso-mercuric Sulphate.—Obtained by gently heating mercuroso-mercuric nitrate with sulphate of soda. Insoluble in cold water.

Hydrochloric acid decomposes it without the aid of heat, and separates mercurous chloride.

| | | | | Brooke. | | |
|---|---|---|---|---|---|---|
| $2Hg^2O$ | 416 | 44·88 | | 44·45 | 44·21 | 44·50 |
| $4HgO$ | 432 | 46·58 | | 46·84 | 46·84 | 46·26 |
| $2SO^3$ | 80 | 8·54 | | 8·56 | 8·60 | |
| $2Hg^2O,SO^3+4HgO,SO^3$ | 928 | 100·00 | | 99·85 | 99·65 | |

(Brooke, *Pogg.* 66, 63.) ¶

G. Mercuric Sulphocarbonate.—Hydrosulphocarbonate of ammonia forms with mercuric salts a yellow precipitate, which changes in the course of a few hours, with separation of sulphide of carbon, first to orange, and then to greyish black; if quickly dried in vacuo, it is afterwards resolved by heat into cinnabar and bisulphide of carbon. (Zeise.) Berzelius, by mixing sulphocarbonate of calcium with a mercuric salt, obtained a black precipitate, which dissolved in excess of the precipitant, and in drying gave off sulphide of carbon, and was converted into black sulphide of mercury.

H. Mercuric Hyposulphophosphite.—*a. Bibasic.*—2HgS,PS.—Formed by heating the compound I in a retort. At first, the compound K sublimes, and a dark mass is left, which, at a stronger heat, likewise sublimes completely in the form of 2HgS,PS. The latter forms shining crystals, of a lighter red than cinnabar, and yielding an orange-yellow powder. (Berzelius.)

*b. Monobasic.*—HgS,PS.—Finely pounded cinnabar, heated in the bulb-apparatus (V. 26) with protosulphide of phosphorus, absorbs the latter, with slight evolution of heat. The excess of sulphide of phosphorus is distilled off in a current of hydrogen gas; if too strong a heat be applied, globules of mercury separate out.—Closely aggregated, dingy-red mass, yielding a brownish yellow powder. When exposed to the air, it becomes nearly black and then yields a blackish grey powder. (Berzelius, *Ann. Pharm.* 46, 256). For the decompositions by heat, *vid. inf.*

I. Mercuric Sulphosphosphite.—$2HgS,PS^3$.—Remains in the form of a yellowish white body, when HgS,PS is heated in a retort for a long time, at a temperature not exceeding the boiling point of sulphur, a black mass chiefly consisting of globules of mercury, likewise subliming at the same time. The yellowish white substance, when heated till it volatilizes, is resolved into H, *a*, and K.

$$2(2HgS,PS^3)=2HgS,PS+2HgS,PS^5.$$

(Berzelius, *Ann. Pharm.* 46, 265.)

K. Mercuric Sulphophosphate.—$2HgS,PS^5$.—Formed by subliming HgS,PS in a retort at a temperature higher than that required for the formation of the sulphophosphite. At first, mercury sublimes in the neck of the retort, which must be closed and kept warm; afterwards, the compound K is evolved, and forms a sublimate, crystalline throughout its whole mass, and partly consisting of delicate, highly lustrous, transparent, pale yellow needles.—2. By heating the sulphophosphite, whereupon K sublimes before the compound H, *a*. (Berzelius, *Ann. Pharm.* 46, 279.)

L. Sulphate of Mercuric Oxide with Phosphide of Mercury.—Phosphuretted hydrogen gas passed through an aqueous solution of acid mercuric sulphate, produces a heavy yellow precipitate, which soon turns white; it must be washed with cold water, pressed between blotting paper, and then dried in vacuo over oil of vitriol. After drying it is yellow, but on exposure to the air absorbs water and turns white again. When heated in a retort, it makes a slight crackling noise, and gives off, first a large quantity of sulphurous acid gas, then vapour of mercury, then sulphuric acid vapour, and leaves fused hydrate of phosphoric acid. It dissolves completely in aqua-regia. (H. Rose, *Pogg.* 40, 75.)

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| 9Hg | 900·0 | .... | 76·57 | .... | 76·25 |
| P | 31·4 | .... | 2·67 | .... | 2·31 |
| $4SO^3$ | 160·0 | .... | 13·61 | .... | 13·19 |
| 6O | 48 0 | .... | 4·09 | .... | |
| 4HO | 36·0 | .... | 3·06 | .... | |
| | 1175·4 | .... | 100·00 | | |

$Hg^3P + 2(3HgO,2SO^3)4Aq$.—It is therefore a compound of triphosphide of mercury with sesquibasic mercuric sulphate, a compound not known in the separate state. (H. Rose). Hopkins (*Sill. Amer. J.* 18, 364) states that he has obtained the sesquibasic sulphate in the free state.

M. Sulphate of Mercuric Oxide with Sulphide of Mercury.—Formed when an aqueous solution of acid mercuric sulphate is treated with a quantity of sulphuretted hydrogen not sufficient to decompose it completely. The white precipitate acquires a yellowish tint by washing. (H. Rose). ¶. According to Jacobsen (*Pogg.* 68, 411), the precipitate, when washed with cold water, remains white after drying in the water-bath, merely exhibiting a faint yellowish tinge on the surface; when washed with boiling water, however, it gradually acquires a yellowish colour, but undergoes no further change after drying at 100°.

| | | | | | Jacobsen. | | |
|---|---|---|---|---|---|---|---|
| | | | | | *a.* | | *b.* |
| 3Hg | 300 | .... | 80·80 | .... | 79·01 | .... | 80·87 |
| 2S | 32 | .... | 8·56 | .... | 8·91 | .... | 8·99 |
| 5O | 40 | .... | 10·64 | .... | 12·08 | .... | 10·14 |
| $HgS + 2HgO,SO^3$ | 372 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

*a* was washed with cold, *b* with boiling water. ¶

## Mercury and Selenium.

A. Selenide of Mercury.—The two substances, when heated together, combine without emission of light.—*a.* When excess of mercury is used and the uncombined portion distilled off, there remains a solid, tin-white compound, which, at a high temperature, sublimes in metal-shining laminæ, without previously fusing.—*b.* When mercury is heated with excess of selenium, a portion of the latter element sublimes at first, then a grey, less distinctly crystalline substance, which is either a perselenide of mercury, or a mixture of the compound *a* with free selenium;—and lastly a sublimate of *a* is formed.—Selenide of mercury dissolves readily in cold aqua-regia, forming a solution of mercuric selenite; by

continued boiling with nitric acid, it is converted into mercurous selenite, which presents the appearance of a white powder, whilst a small portion of selenious acid remains dissolved in the nitric acid. (Berzelius.)

B. Selenite of Mercurous Oxide, or Mercurous Selenite.—Selenious acid and alkaline selenites give a precipitate with mercurous nitrate.—White powder; when heated, it fuses into a dark brown substance, which becomes lemon-yellow on cooling; at a stronger heat, it boils, and passes over in brown drops, which become amber-yellow and mostly transparent on cooling. Hydrochloric acid converts it into protochloride of mercury, the selenious acid being partly reduced to the state of free selenium, and partly remaining dissolved in the liquid. The salt gives up all its acid to caustic potash. It is not soluble either in water or in aqueous selenious acid. (Berzelius.)

C. Selenite of Mercuric Oxide, or Mercuric Selenite.—*a. Monoselenite.*—Formed by double decomposition, or by bringing mercuric oxide in contact with aqueous selenious acid.—White powder, insoluble or very slightly soluble in water.

*b. Biselenite.*—Formed by adding mercuric oxide to aqueous selenious acid, till the monobasic salt begins to separate out—then filtering and evaporating. Large prisms, longitudinally striated, having the taste of corrosive sublimate; they contain a large quantity of water. The crystallized salt fuses in its water of crystallization when heated, then solidifies, and finally sublimes unaltered. Easily soluble in water, very slightly in alcohol; the aqueous solution is not precipitated by ammonia, and very slowly by alkaline carbonates; potash also throws down only part of the oxide. Sulphurous acid precipitates white mercurous selenite, which soon acquires a scarlet colour, from the presence of reduced selenium. (Berzelius.)

D. Sulphoselenide of Mercury. — Massive, granular, soft, of blackish lead-grey colour inclining to steel-grey, like Fahl-ore; it yields a black powder. May be completely sublimed in the form of a black crystalline powder. When ignited with carbonate of soda, it yields metallic mercury. Burns with a blue flame. Fuses immediately on charcoal, emitting white vapours, having an odour of sulphurous acid at first, but afterwards that of selenium, and leaves on the charcoal a white incrustation, which, by continued blowing, is converted into white crystalline mercuric selenite. Imparts a flesh colour to borax. Chlorine gas has no action on it in the cold, but, on the application of heat, easily converts it into chloride of sulphur, chloride of selenium, and chloride of mercury. By hydrochloric acid, and even by cold nitric acid, it is but slightly if at all affected; but cold aqua-regia attacks it very quickly, separating cochineal-coloured flakes of sulphide of selenium, which fuse together into drops when heated. (*Kastn. Arch.* 14, 127; H. Rose, 46, 315.)

| | | | | | H. Rose. From Mexico. |
|---|---|---|---|---|---|
| 5Hg | 500 | .... | 82·78 | ..... | 81·33 |
| Se | 40 | .... | 6·62 | ..... | 6·49 |
| 4S | 64 | .... | 10·60 | ..... | 10·30 |
| HgSe + 4HgS | 604 | .... | 100·00 | ..... | 98·12 |

## Mercury and Iodine.

A. Diniodide of Mercury, or Mercurous Iodide.—*Protoiodure de Mercure.*—*Preparation.*—1. By triturating 2 At. mercury with 1 At. iodine:—it is best to add a little alcohol—200 parts of mercury triturated with 126 of iodine yield a reddish mixture, which, on the addition of a small quantity of alcohol (which dissolves the iodine and transfers it to the mercury), assumes a yellowish colour, the mercury and iodine quickly disappearing. (Berthemot, *J. Pharm.* 17, 456.)—Even when only 124 parts of iodine are taken with 200 of mercury, and rubbed up with a small quantity of alcohol, the greenish-yellow mixture still contains protiodide of mercury, which may be dissolved out by alcohol. 200 parts of mercury triturated with only 100 parts of iodine yield a darker, grass-green iodide. (Berthemot, *N. J. Pharm.* 4, 36.)—Boiling alcohol extracts a small quantity of mercuric iodide, even from the preparation made with 200 parts of mercury and 100 of iodine, but less than when higher proportions of iodine are used. (Soubeiran, *Ibid.*)—If water be added to the mixture instead of alcohol, the mercury and iodine combine slowly in the cold, but quickly when heated, forming a brown-red powder, which soon turns yellowish-green on being triturated with alcohol. When 200 parts of mercury are triturated with 125 parts of somewhat moist iodine, without further addition, the mixture becomes heated in consequence of the combination which ensues, so that the mass liquefies, with evolution of iodine vapours, and afterwards solidifies in the form of a brown-red slag, which is difficult to pulverize by itself, but, on the addition of alcohol, is soon converted into a yellowish-green powder. (Silber, *N. Br. Arch.* 28, 62.)—2. By triturating 1 At. protiodide of mercury with 1 atom of metallic mercury.—Berthemot recommends 226 pts. protiodide to 100·6 mercury, with the addition of a little alcohol.—3. By decomposing mercurous nitrate, or, better, dichloride of mercury or mercurous acetate with hydriodic acid, or, better, with iodide of potassium:

$$Hg^2O,NO^5 + KI = Hg^2I + KO,NO^5.$$

Since mercurous nitrate is not soluble in water, except through the medium of a certain excess of acid, and since this excess remains uncombined unless the iodide of potassium contains caustic potash or carbonate of potash, an oxidizing action will be thereby exerted, and, if the liquid be not quickly filtered, the diniodide of mercury will be converted into protiodide, the admixture of which will change the colour of the precipitate from green to yellow. This effect is produced in a still greater degree when hydriodic acid is used, for the whole of the nitric acid is then set free. The mercurous nitrate is likewise frequently contaminated with mercuric nitrate, which immediately gives a precipitate of protiodide. The liquids must be mixed in equivalent proportion, because an excess of iodide of potassium converts a portion of the precipitated diniodide of mercury into protiodide, which dissolves, and metallic mercury, which remains mixed with the precipitate; but a slight excess of iodide of potassium is useful to dissolve the protiodide of mercury formed by the nitric acid, and thereby restore the green colour of the precipitate. (Inglis, N. E. Henry, *N. J. Pharm.* 13, 40; Berthemot; Boullay.)—Dichloride of mercury triturated with aqueous iodide of potassium yields pure green diniodide of mercury. (Inglis, *Phil. Mag. J.* 8, 17.) $Hg^2Cl + KI = Hg^2I + KCl$. The two compounds must be mixed in the exact stoichiometric proportions of 235·4 $Hg^2Cl$ to 165·2 KI; for an excess of calomel would remain undecomposed and mix with the mercurous

iodide, and an excess of iodide of potassium would separate metallic mercury.—The solution of mercurous acetate in cold water yields, with iodide of potassium, a green precipitate of pure mercurous iodide (P. Boullay); but the mercurous acetate is but sparingly soluble in cold water; and hot water partially decomposes it into mercuric acetate, which dissolves, and metallic mercury, which is separated. It is best, therefore, to triturate crystallized mercurous acetate in the cold with aqueous iodide of potassium, whereby a greenish-black powder is first produced, and afterwards a fine yellowish-green powder; it is apt, however, to be mixed with undecomposed mercurous acetate, which cannot be extracted by cold water, and is resolved by hot water into mercuric acetate and metallic mercury—the latter remaining mixed with the mercurous iodide. (Berthemot.) [If exactly 259 pts. (1 At.) of mercurous acetate are used with 165·2 pts. (1 At.) of iodide of potassium, and left to act for some time, this admixture of mercurous acetate in the product need not be feared.] Protiodide of iron is likewise recommended instead of iodide of potassium for preparing the diniodide of mercury.—The green precipitate obtained by either of these methods is washed with hot water and dried in the shade.

*Properties.* Green powder (Inglis); dark green, according to Boullay; yellowish-green, according to Berthemot. Sp. gr. of the powder dried by a strong heat, 7·6645 (Karsten); 7·75 (Boullay).

| | | | |
|---|---|---|---|
| 2Hg | 200 | ..... | 61·35 |
| I | 126 | ..... | 38·65 |
| $Hg^2I$ | 326 | ..... | 100·00 |

Diniodide of mercury, when exposed to light, becomes dark green and black. The darkening of colour takes place only when the compound is moist, in which case no free iodine is evolved, but hydriodic acid; probably, therefore, mercurous oxide becomes mixed with the residue. (Artus, *J. pr. Chem.* 8, 63.) When kept for a few weeks in vessels containing air, even though quite impervious to light, the diniodide of mercury is resolved into metallic mercury and protiodide, which forms dendritic excrescences; the decomposition does not take place under water. (Inglis.) When sublimed, it is resolved into metallic mercury, which collects at the top, and a greenish-yellow sublimate, consisting of $Hg^4 I^3$, which settles below it. (Labouré, *N. J. Pharm.* 4, 329.) When immersed in solution of protochloride of tin, it gradually turns greenish-black, then black, and lastly slate-grey, in consequence of stannic oxide becoming mixed in considerable quantity with the black powder. (Labouré.) It dissolves in ammonia, leaving a grey residue [of mercury?]. (Wittstein, *Repert.* 63, 322.) With aqueous hydriodic acid or iodide of potassium, it is resolved into protiodide of mercury which dissolves, and metallic mercury which remains behind. A similar action is produced at a boiling heat by the aqueous iodides of sodium, barium, calcium, magnesium, and zinc. (P. Boullay; Labouré.) Boiling hydrochloric acid exhibits the same action, though very slowly; moreover, it requires frequent renewal. (Boullay.) The boiling solution of sal-ammoniac or common salt, likewise takes up a small quantity of protiodide of mercury, and separates metallic mercury. (Boullay.) The iodide is converted into chloride, and thereby dissolved. (Mialhe.) Diniodide of mercury dissolves in more than 2375 parts of water (Saladin, *J. Chim. méd.* 7, 530), but not in alcohol.

B. Three-fourths Iodide of Mercury, or Mercuroso-mercuric Iodide.—This yellow compound was formerly taken by Gay-Lussac, Colin, and others, for diniodide of mercury, till Inglis, Boullay, and others, showed that it is richer in iodine. *Preparation.* 1. By precipitating a solution of mercurous nitrate with hydriodic acid or iodide of potassium, and not collecting the precipitate on the filter till the green colour has changed to yellow.—2. By dissolving in aqueous iodide of potassium half the quantity of iodine which it already contains, and adding that solution to a solution of mercurous nitrate. The precipitate first formed consists of red iodide of mercury, but it turns yellow on agitation. If too much of the solution of iodide of potassium containing excess of iodide has been added, the precipitate remains mixed with protiodide of mercury, which, however, may be readily dissolved out by alcohol. (P. Boullay.)

Yellow powder, which turns red whenever it is heated. (Colin.) May be fused, and sublimes undecomposed on a sudden application of heat. (Colin.) Acquires a dark carmine tint when heated, and afterwards sublimes in dark, carmine-coloured crystals, which again turn yellow on cooling. (Inglis.)

| | | | | | Boullay. |
|---|---|---|---|---|---|
| 4Hg | 400 | .... | 51·41 | .... | 51·9 |
| 3I | 378 | .... | 48·59 | .... | 48·1 |
| $Hg^4I^3$ | 778 | .... | 100·00 | .... | 100·0 |

Becomes dark and greenish when exposed to light. (Colin, Inglis.) If exposed to light under water, it forms a few small cubes of mercuric iodide. In the dark, it remains undecomposed. (Inglis.) Aqueous hydriodic acid, and the aqueous compounds of iodine with the alkali-metals, magnesium, and zinc, abstract mercuric iodide from it at first, and convert it into green mercurous iodide, which is then dissolved, with separation of mercury. (Boullay.) Alcohol extracts no mercuric iodide from the yellow compound—a proof that it is not a mere mixture of mercurous and mercuric iodide. (Boullay.)

C. Protiodide of Mercury, or Mercuric Iodide.—*Deuto-iodure de Mercure.*—Del Rio (*Schw.* 51, 253) attributes this composition to a mineral found in Mexico, resembling cinnabar, but having a lighter streak. It forms a magnificent water-colour, known by the name of *scarlet,* which, however, fades very quickly when exposed to light, and at the same time destroys the colour of vermilion which may be mixed with it. It is likewise used in calico-printing.

*Formation.* 1. When 1 At. mercury is triturated with 1 At. iodine. ¶ According to Mohr (*Arch. Pharm.* [2], 55, 29), iodine and mercury, when triturated together in exact equivalent proportion, do not unite completely in the form of mercuric iodide; but the resulting mass contains free iodine, which escapes when the product is dried over the water-bath, and mercurous iodide, which, when sublimed, is resolved into mercuric iodide and metallic mercury. ¶—2. When a mercuric salt is precipitated by hydriodic acid or a dissolved metallic iodide, such as iodide of potassium or iodide of iron:

$$HgO,NO^5 + KI = HgI + KO,NO^5.$$

Or:

$$HgCl + KI = HgI + KCl.$$

3. When iodine is triturated with mercurous oxide and water, or with solution of mercurous nitrate, mercuric oxide being formed at the same time; or when iodine is triturated with mercuric nitrate:

$$Hg^2O + I = HgI + HgO.$$

4. When iodine is triturated with mercuric oxide and water, a large quantity of [oxygen] gas-bubbles being given off at the same time. (Vauquelin.) Rammelsberg, on the contrary (*Pogg.* 48, 182), on boiling mercuric oxide with iodine and water, obtained a solution of mercuric iodide mixed with iodate.—5. When iodine is triturated with mercuric nitrate—whereupon no gas is evolved, and a pale precipitate containing oxygen is obtained. (Vauquelin.) It is probable that mercuric iodate becomes mixed with the iodide in this process:

$$6(HgO,NO^5) + 6I = 5HgI + HO,IO^5 + 6NO^5.$$

6. When iodine is triturated with dichloride of mercury and with water, which takes up the protochloride of mercury produced in the process. (Landerer.)—7. When iodine is triturated with cyanide of mercury, iodide of cyanogen being formed at the same time. 8. When diniodide of mercury is brought in contact with iodine or its aqueous solution. 9. When diniodide of mercury is triturated and heated with water and teriodide of arsenic, the action being attended with reduction of arsenic. (Soubeiran, *J. Pharm*, 27, 744.)

*Preparation.* 1. By triturating 1 At. mercury with 1 At. iodine, the mixture being moistened with water or alcohol. 100 parts of mercury triturated with 124·7 parts of iodine, and frequently moistened with a very small quantity of alcohol, yields a red mixture, the colour of which is inferior to that obtained by (2); if too much alcohol is used, the combination is attended with a rise of temperature, which causes the mass to fuse, and the iodine to evaporate. (Berthemot, *J. Pharm.* 17, 456.) ¶ Dublanc (*N. J. Pharm.* 15, 64) pours a kilogramme of alcohol on 100 grammes of mercury, and adds 124 grammes of iodine in successive portions of 10 grammes each, agitating after each addition till the alcohol becomes perfectly colourless; after the addition of the last 4 grammes, the alcohol remains coloured, because the whole of the mercury is then converted into iodide. The preparation is washed with alcohol; it is crystalline, and of a hyacinth-red colour. ¶—2. By precipitating an aqueous solution of mercuric nitrate or chloride with hydriodic acid, iodide of potassium, or protiodide of iron, and washing the precipitate with water. Unless the materials are mixed in exactly equivalent proportions, part of the iodide of mercury remains dissolved in the excess of the mercuric salt, or of the iodide of potassium. (Boullay.)

*Properties.* Protiodide of mercury is dimorphous, its form varying with the temperature.

*a. Red modification.* Both the preceding modes of preparation yield the compound in the form of a scarlet powder. By dissolving this powder to saturation in a boiling, moderately-dilute solution of iodide of potassium, and leaving it to cool (Boullay, Mitscherlich)—or in boiling aqueous iodide of zinc, and evaporating in vacuo (Inglis)—or by dissolving iodine to saturation in solution of mercuric nitrate, keeping the liquid boiling all the while, and replacing the water as it evaporates, and leaving the solution to cool,—the mercuric iodide is obtained in definite crystals. Crystalline system, the square prismatic. Acute square-based octohedrons (Fig. 21), but always with truncated summits: $e : e'' = 141°$; $p : c = 109° 30'$. (Mitscherlich, *Pogg.* 28, 117.) According to this statement, the cubes and prisms observed by Boullay and Inglis must be

regarded as square prisms of different lengths. Specific gravity, 6·2009 (Karsten), 6·320 (Boullay). Fuses readily into a dark amber-yellow liquid (Warington), which on cooling solidifies in a yellow crystalline mass, in which the iodide of mercury has assumed the form *b;* this, when cooled to a lower temperature, resumes its bright red colour, not gradually but suddenly; individual crystals which have remained yellow even after perfect cooling, immediately turn red on touching them with the fingers, or agitating the paper on which they lie. (Mitscherlich.) According to Mather (*Sill. Amer. J.* 27, 263), the fused mass, immediately after solidification, exhibits a red colour, which afterwards turns yellow and remains so, but is immediately reddened by contact with potash-ley. It volatilizes easily without decomposition, and sublimes in yellow crystals, *b;* by very careful heating, red square-based octohedrons may likewise be sublimed, together with the yellow crystals. (Warington.)

*b. Yellow modification.*—Produced from *a* by fusion and cooling, or by sublimation; but the crystals pass suddenly into the yellow modification even at a heat at which they neither fuse nor sublime. (Mitscherlich.) When mercuric salts are precipitated by iodide of potassium, the modification *b* is likewise thrown down in the form of a yellow powder, which afterwards changes into the scarlet variety *a*. The precipitate obtained with chloride of mercury, appears at first, when examined by the microscope, to be composed of rhombic laminæ, which are colourless by transmitted, and yellow by reflected, light; these, however, gradually alter in form by truncation of the edges and corners, as if they were dissolving, their dimensions being thereby continually reduced until they ultimately disappear, and red, square-based octohedrons are produced in their place. (Warington, *Phil. Mag. J.* 21, 192.) Crystalline system the right prismatic (Fig. 61); $u : u' = 114°$. (Mitscherlich.) The prisms are shortened into tables; (according to Frankenheim, they belong to the oblique prismatic system). Colour, lemon-yellow. At ordinary temperatures, the yellow crystals are converted into the red by very slight causes. [Compare the observations of Hayes and Frankenheim (I. 100).] If one of the rhombic laminæ be observed under the microscope while it is turning red, it will be found that the red colouring progresses by sudden starts, and is always bounded by a line parallel either to a lateral face or to a diagonal. (Warington, *Phil. Mag. J.* 21, 192.)

| | | | | | | Vol. | | Sp. gr. |
|---|---|---|---|---|---|---|---|---|
| Hg | 100 | 44·25 | | Vapour of mercury | | 1 | | 6·9300 |
| I | 126 | 55·75 | | Vapour of iodine | | 1 | | 8·7356 |
| HgI | 226 | 100·00 | | Vapour of mercuric iodide | | 1 | | 15·6656 |

Potassium triturated with iodide of mercury abstracts the iodine, the action being attended with evolution of light and heat. (Rammelsberg, *Pogg.* 48, 180.) Many of the heavy metals, either alone or with the aid of water, withdraw all or half the iodine; and the resulting metallic iodide sometimes unites with part of the iodide of mercury, forming an iodine-salt. When mercuric iodide is heated and triturated with different metals and water, the following results are obtained :—*Zinc:* great evolution of heat, with formation of iodide of zinc and zinc-amalgam.—*Cadmium:* decomposition, attended with formation of iodide of mercury and cadmium. *Tin:* decomposition takes place slowly, after half an hour's boiling, tin-amalgam forms, and stannic oxide is precipitated (in consequence of access of air), but the liquid still contains undecomposed protiodide of mercury,

besides protiodide of tin.—*Iron:* diniodide of mercury is first produced, with slight rise of temperature; afterwards, especially if heat be applied, metallic mercury separates, while protiodide of iron, together with a certain quantity of undecomposed protiodide of mercury, dissolves in the liquid.—*Copper:* diniodide of mercury is first formed; then, after long boiling, metallic mercury separates, together with diniodide of copper. *Lead* or *Silver:* diniodide of mercury, together with iodide of lead or iodide of silver.—*Bismuth* or *Antimony*, finely pounded and boiled with water; the liquid contains acid hydriodate of bismuth-oxide or antimonic oxide, with a small quantity of iodide of mercury. (Berthemot, *J. Pharm.* 14, 610.) Protiodide of mercury immersed in aqueous protochloride of tin is decomposed, and continues to part with its iodine—becoming first yellowish-red, then yellow ($Hg^4I^3$), then greenish-yellow, then green ($Hg^2I$), till it is ultimately converted into a mixture of metallic mercury and stannic oxide. (Labouré.) Mercuric iodide yields with aqueous ammonia a brown powder and a yellow liquid, which deposits snow-white flakes (Böttger, *J. pr. Chem.* 8, 481); when immersed in ammonia, it turns white, and afterwards brown-red when heated. (Wittstein, *Repert.* 63, 322.) Fixed alkalis, in the state of solution, separate mercuric oxide from the iodide (or if very dilute, a compound of the oxide and iodide: *Rammelsberg*), and form a soluble compound of iodide of mercury with the iodide of the alkali-metal. When mercuric iodide is boiled with aqueous potash, mercuric oxide separates out, and there is formed a yellowish solution of iodide of mercury and iodide of potassium [$4HgI + KO = HgO + KI, 3HgI$], which, on cooling, first deposits HgI, and then greenish-yellow needles of KI, 2HgI. Alcoholic potash acts in the same manner, but still more easily. Soda, baryta, and strontia behave in a similar manner, and yield iodine-salts. Lime also produces a similar effect, when boiled with alcohol; but if water be substituted for the alcohol, no decomposition takes place. Similarly, carbonate of potash or soda does not decompose mercuric iodide, when boiled with it in water, but when alcohol is used, the decomposition is produced; the alcohol appears to favour the action by its solvent power. Magnesia, carbonate of magnesia, and alumina produce no decomposition in the humid way. (Berthemot, *J. Pharm.* 14, 186.) Mercuric iodide dissolves in aqueous chloride of lime, when the solution is heated, and as it begins to boil deposits basic periodate of lime in the form of a white jelly, while protochloride of mercury dissolves in the liquid. (Rammelsberg, *Pogg.* 48, 182.) When chlorine gas is passed through water in which iodide of mercury is diffused, a bright yellow solution is formed, containing protochloride of mercury and terchloride of iodine. (Filhol.)

Protiodide of mercury is very sparingly soluble in water. The solution, left to evaporate freely, deposits brownish, microscopic, acute, six-sided crystals, and obtuse rhombohedrons, probably consisting of mercuric oxide. (Saladin, *J. Chim. méd.* 7, 530.) It dissolves in many aqueous acids, viz., in hydriodic and hydrochloric acid; also in many ammoniacal salts, and in aqueous chloride of potassium. It dissolves completely in hot aqueous carbonate or sulphate of ammonia, and even in cold hydrochlorate or succinate of ammonia (Wittstein); also in cold nitrate of ammonia. (Brett.) The solution in hot sal-ammoniac deposits part of the mercuric iodide in needles as it cools, and the rest when diluted with water. On boiling with sal-ammoniac and alcohol, a solution is obtained, which deposits nothing on cooling, but yields crystals of mercuric iodide when evaporated, and is precipitated by water. (Böttger.) 226 pts.

(1 At.) of mercuric iodide dissolve in a hot, saturated, aqueous solution of 387 pts. (5 At.; 5 . 74·6 = 373) of chloride of potassium; during the cooling of the solution (which is precipitated yellow by water), the greater part of the iodide of mercury separates out in crystals, which are yellow at first, but soon turn red; the mother-liquid, when diluted with water, still deposits a small quantity of mercuric iodide, so that the filtrate is but slightly browned by an alkaline hydrosulphate. A similar reaction is produced by sal-ammoniac. (P. Boullay, *Ann. Chim. Phys.* 34, 364.) Protiodide of mercury likewise dissolves in aqueous hydrochlorate, nitrate, or acetate of mercuric oxide—in aqueous solutions of the metallic iodides, with which it forms iodine-salts, the compounds which Bonsdorff calls *Iodo-hydrargyrates*—in hot alcohol, from which it crystallizes on cooling—and sparingly in ether.

D. Mercuric Oxy-iodide.—$3HgO,HgI$.—1. Formed by fusing 3 At. mercuric oxide with 1 At. mercuric iodide.—2. Mercuric iodide heated with dilute potash leaves a small quantity of a yellowish-brown powder, consisting of mercuric oxy-iodide, generally mixed with mercuric oxide. This powder, if exposed to a current of ammoniacal gas, after being dried at 120°, gives off water and yields a red-brown compound = $Hg,NH^2,HgI$, $2HgO$. (Rammelsberg, *Pogg.* 48, 182.)

$$3HgO,HgI + NH^3 = HgNH^2,HgI,2HgO + HO.$$

E. Iodide of Mercury and Hydrogen, or Acid Hydriodate of Mercuric Oxide.—1. The concentrated aqueous solution of 127 pts. (1 At.) hydriodic acid dissolves, when heated, 456 pts. (2 At.; 2 . 226 = 452) of mercuric iodide. Of this quantity it deposits, on dilution with water, 228 pts. (1 At.), so that 228 pts. (1 At.) of mercuric iodide remain dissolved in the hydriodic acid. If the heated solution be left to cool without the addition of water, mercuric iodide crystallizes out first, and subsequently the liquid deposits yellow transparent needles. The mother-liquid, on dilution with water, deposits an additional quantity of mercuric iodide. The same needles are obtained by dissolving iodide of mercury in warm aqueous hydriodic acid, and evaporating the solution in dry, and somewhat rarefied air. In warm dry air, they give off hydriodic acid, and are converted into red iodide of mercury. Water separates red iodide of mercury from them, taking up the hydriodic acid in combination with a small quantity of iodide of mercury. Hence the needles are resolved, even in common air, into iodide of mercury and aqueous hydriodic acid (still containing iodide of mercury). (P. Boullay, *Ann. Chim. Phys.* 34, 340.) [Probably the crystals, like the saturated, concentrated solution, are composed of $2HgI,HI$,—or, if they contain water, of $2HgO,3HI$. Boullay gives another formula.]

*Biniodide of Mercury*, $HgI^2$, is said by Hunt (*Phil. Mag. J.* 12, 27; also *J. pr. Chem.* 14, 120) to be obtained by precipitating aqueous protochloride of mercury with aqueous iodide of potassium, previously saturated with iodine. The purple-brown precipitate, which contains 27·9 parts of mercury to 72·1 of iodine, is converted into red iodide of mercury by heat or by exposure to the air, &c. [Probably a mere mixture of mercuric iodide with iodine.]

F. Iodate of Mercurous Oxide, or Mercurous Iodate.—Iodic acid or iodate of potash forms with dissolved mercurous nitrate, a white

precipitate having a pearly lustre. (Vauquelin.) If the mercurial solution does not contain too much free acid, the mercury is completely precipitated by an equivalent quantity of iodate of soda. (Rammelsberg.) The salt is anhydrous and volatilizes completely when heated, being resolved into mercuric iodide, metallic mercury (mercuric oxide: *Lefort*), and oxygen gas (Rammelsberg, *Pogg.* 44, 570):

$$Hg^2O + IO^5 = HgI + Hg + 6O.$$

It dissolves easily and completely in dilute hydrochloric acid, giving rise to an evolution of chlorine (Rammelsberg); according to Lefort (*N. J. Pharm.* 8, 5), it is converted into chloride of iodine, protochloride of mercury, and free chlorine. Ammonia added to the hydrochloric acid solution forms a precipitate of iodide of nitrogen. It dissolves, but not very freely, in nitric acid (Rammelsberg), being thereby converted into the mercuric salt (Lefort). It is soluble in iodic acid, and to a very slight degree in water. (Pleischl.)

G. Iodate of Mercuric Oxide, or Mercuric Iodate.—Iodic acid and iodate of potash or soda give no precipitate with mercuric salts. (Pleischl, Rammelsberg.) If mercuric oxide precipitated by potash and then washed, be heated, while yet in the moist state, with aqueous hydriodic acid, it does not dissolve, but is quickly converted into white, pulverulent mercuric iodate. The oxide prepared by ignition is not affected by iodic acid. The salt is anhydrous, and when heated, gives off oxygen and is completely converted into protiodide of mercury. With hydrochloric acid, it behaves in the same manner as the mercurous salt. Stannous sulphate added to the solution throws down red iodide of mercury, which is then converted into the yellow modification. (Rammelsberg, *Pogg.* 44, 570.)

| | | | | | Rammelsberg. |
|---|---|---|---|---|---|
| $HgO$ | 108 | .... | 39·42 | .... | 39·83 |
| $IO^5$ | 166 | .... | 60·58 | .... | 60·17 |
| $HgO,IO^5$ | 274 | .... | 100·00 | .... | 100·00 |

H. and I. Mercurous and Mercuric Periodates.—Periodate of soda forms with mercurous nitrate a yellow precipitate, which, when gently heated, gives off water and assumes a brown-red colour; with mercuric nitrate, the same reagent gives a white precipitate which becomes yellowish when heated. Both these precipitates are easily soluble in dilute nitric acid. (Benckiser, *Ann. Pharm.* 17, 259.)

K. Mercuric Iodo-sulphide.—$HgS,HgI$.—When protiodide of mercury is digested for a considerable time with a quantity of sulphuretted hydrogen water, not sufficient for its complete decomposition, a yellow powder is obtained, which, on account of its lightness, may easily be separated from the undecomposed iodide by levigation; when heated, it first yields a sublimate of mercuric iodide and then of mercuric sulphide. (H. Rose).—2. From a solution of mercuric oxide and mercuric iodide in hydrochloric acid, a small quantity of sulphuretted hydrogen throws down an orange-yellow precipitate of iodo-sulphide of mercury, which, by a larger quantity of sulphuretted hydrogen, is converted into black mercuric sulphide. (Rammelsberg, *Pogg.* 48, 175.)

L. Mercuric Iodo-sulphate.—$HgI + HgO,SO^3$.—Formed, with evo-

lution of sulphurous acid, when diniodide of mercury is heated with sulphuric acid; it crystallizes out as the liquid cools:

$$Hg^2I + 2SO^3 = HgI + HgO,SO^3 + SO^2.$$

If protiodide of mercury be used, vapours of iodine are given off at the same time. The crystals may be washed with strong alcohol without decomposition, but water decomposes them. When heated, they are resolved into mercuric iodide, which sublimes, and mercuric sulphate, which remains behind. (Souville, *J. Pharm.* 26, 174.)

### Mercury and Bromine.

A. Dibromide of Mercury, or Mercurous Bromide.—1. Formed by subliming an intimate mixture of 1 At. mercury and 1 At. protobromide of mercury. (Löwig.)—2. By precipitating mercurous nitrate with aqueous bromide of potassium. (Balard.) When prepared by the first process, it forms a fibrous mass (Löwig); long needles which are yellow while hot, but become whitish on cooling. (O. Henry, *J. Pharm.* 15, 56.) By (2): white powder (Balard); yellowish white flakes. (O. Henry.) Specific gravity, 7·307. (Karsten.) Fusible (O. Henry); volatilizes undecomposed at a low red heat. (Löwig.) Tasteless and inodorous.

| | | | | | Vol. | | Sp. gr. |
|---|---|---|---|---|---|---|---|
| 2Hg | 200·0 | .... | 71·84 | Vapour of mercury | 1 | .... | 6·9300 |
| Br | 78·4 | .... | 28·16 | Vapour of bromine | ½ | .... | 2·7177 |
| $Hg^2Br$ | 278·4 | .... | 100·00 | Vapour of mercurous bromide | 1 | .... | 9·6477 |

When heated with phosphorus, it is resolved into bromide of phosphorus and phosphide of mercury. (Löwig.) Treated with cold aqueous ammonia, and then washed with water containing ammonia, it leaves a grey powder, which contains globules of mercury; and when heated, gives off ammonia, and yields a sublimate of mercury, dibromide, and protobromide of mercury. (Rammelsberg.) With caustic potash, it yields mercurous oxide and bromide of potassium. When boiled with aqueous hydrobromate or hydrochlorate of ammonia, it yields a solution of protobromide of mercury, with a residue of metallic mercury. (Löwig.) It is not perceptibly soluble in cold carbonate, hydrochlorate, or succinate of ammonia; while the same liquids, when hot, dissolve it with tolerable facility, leaving, however, a grey pulverulent residue [metallic mercury]; it is not perceptibly soluble in sulphate of nitrate of ammonia, even at a boiling heat. (Wittstein.)

B. Protobromide of Mercury, or Mercuric Bromide.—1. Mercury unites with bromine at ordinary temperatures, the combination being attended with evolution of heat, but not of light. (Balard.)—2. The same compound is formed by agitating mercury with water, adding bromine as long as its colour is destroyed, then boiling, filtering, and leaving the solution to crystallize.—3. By dissolving mercuric oxide in hot aqueous hydrobromic acid, and leaving the solution to crystallize.—4. By subliming mercuric sulphate with bromide of potassium. (Löwig.) The sublimate contains also dibromide of mercury. (O. Henry.) 5. By mixing aqueous mercuric nitrate with bromide of potassium, evaporating as long as bromide of mercury crystallizes out, and purifying the product by solution in

alcohol. The mother-liquid evaporated to dryness leaves a residue, from which boiling alcohol still extracts a small quantity of the compound. (Löwig.) Crystallizes from the aqueous solution in soft, silvery laminæ; from the alcoholic solution in white needles. (Löwig.) The product obtained by (5) has, after drying at a strong heat, a specific gravity of 5·9202. (Karsten.) Fuses when heated (Löwig), and sublimes. (Balard, Löwig.) Its aqueous solution reddens litmus. (v. Bonsdorff.)

| | | | | | Vol. | | Sp. gr. |
|---|---|---|---|---|---|---|---|
| Hg | 100·0 | 56·05 | | Vapour of mercury | 1 | | 6·9300 |
| Br | 78·4 | 43·95 | | Vapour of bromine | 1 | | 5·4355 |
| HgBr | 178·4 | 100·00 | | Vapour of mercuric bromide | 1 | | 12·3655 |

With phosphorus it forms bromide of phosphorus. Heated with antimony or arsenic, it gives up its bromine. Its aqueous solution exposed to sun-light, or placed in contact with mercury or copper, or mixed with dibromide of copper dissolved in hydrobromic acid, deposits dibromide of mercury. (Löwig.) With a small quantity of sulphuretted hydrogen, it yields a white, and with a larger quantity, a black precipitate. (H. Rose.) With ammonia it forms a white, with fixed alkalis a yellow precipitate. (Löwig.) Hypochlorite of soda added to the solution throws down mercuric oxychloride (Rammelsberg); and hypochlorous acid converts protobromide of mercury into protochloride of mercury and bromate of mercuric oxide, the action being attended with evolution of chlorine and bromine. (Balard.) Heated with nitric acid or oil of vitriol, it gives off vapour of bromine. (Balard.) According to H. Rose (*Analyt. Chem.*), it is not decomposed by oil of vitriol. Dissolves in 94 parts of water at 9° (Lassaigne, *J. Chim. méd.* 12, 171), and in 4 or 5 parts of boiling water, the greater part separating out again as the liquid cools. Combines with basic metallic bromides, forming easily soluble bromine-salts, which Bonsdorff calls *Bromo-hydrargyrates*, and losing thereby its power of reddening litmus. (Bonsdorff.) It dissolves very easily in alcohol, and still more easily in ether. (Balard.)

C. Mercuric Oxybromide.—1. The solution obtained by boiling protobromide and protoxide of mercury with water deposits this compound on cooling. (Löwig.)—2. It is also obtained by mixing aqueous bromide of mercury with less than an equivalent quantity of potash, and boiling the liquid with the precipitated oxide. (Löwig.)—3. By precipitating aqueous bromide of mercury with carbonate of soda. (Rammelsberg.) By (1) and (2): lemon-yellow, crystalline powder, which separates from the aqueous solution in yellow spiculæ (Löwig); by (3): dark brown powder. (Rammelsberg, *Pogg.* 55, 248.)

| | | | Rammelsberg. |
|---|---|---|---|
| 4Hg | 400·0 | 79·62 | 80·05 |
| Br | 78·4 | 15·61 | |
| 3O | 24·0 | 4·77 | |
| HgBr, 3HgO | 502·4 | 100·00 | |

At a gentle heat, it is resolved into oxygen gas, a sublimate of dibromide and protobromide of mercury, and a residue of mercuric oxide. (Löwig.) When heated, it yields oxygen gas and a sublimate consisting of metallic mercury and protobromide. By boiling potash, it is wholly converted into pure mercuric oxide. (Löwig.) Does not change in appearance when boiled with potash. (Rammelsberg.) Nitric acid dissolves out

the oxide, and leaves a white residue of mercuric bromide. (Rammelsberg.) Insoluble in cold water, sparingly soluble in hot water, easily soluble in alcohol. (Löwig.) According to Rammelsberg, it is insoluble in alcohol. Did Löwig's compound contain a smaller quantity of oxide?

D. Bromide of Mercury and Hydrogen.—Aqueous hydrobromic acid of specific gravity 1·18, saturated at 40° with bromide of mercury, forms a thickish liquid, which contains 2 atoms of mercuric bromide to 1 atom of hydrobromic acid, and on cooling or dilution with water deposits half its bromide of mercury; so that 1 atom of mercuric bromide remains in combination with 1 atom of hydrobromic acid. 1 At. warm aqueous hydriodic acid and 1 At. cold concentrated hydrochloric acid dissolve 2 At. mercuric bromide; and 1 At. warm concentrated hydrochloric acid dissolves 4 At. mercuric bromide. (Löwig.)

Mercuric oxide digested in bromine-water forms a slightly soluble oxybromide, and a liquid, which, besides a small quantity of oxybromide, contains *hypobromite of mercuric oxide*, or free hypobromous acid, and gives off the latter by distillation in vacuo. (Balard.) If heat be applied, the products formed are protobromide of mercury and bromate of mercuric oxide. (Löwig.)

E. Bromate of Mercurous Oxide, or Mercurous Bromate.—*a. Bibasic.*—Remains undissolved on treating *b* repeatedly with fresh portions of warm, but not boiling water. Lemon-yellow, granular powder, which does not contain water. When heated, it is decomposed with a hissing noise, the greater part being thrown about; the products are free bromine and mercuric oxide. Becomes grey on exposure to light. A small quantity of nitric acid converts it into *b*, which then dissolves in a larger quantity of the acid. (Rammelsberg, *Pogg.* 55, 79.)

| | | | | | Rammelsberg. |
|---|---|---|---|---|---|
| $2Hg^2O$ | 416·0 | .... | 77·84 | .... | 78·41 |
| $BrO^5$ | 118·4 | .... | 22·16 | .... | |
| $2Hg^2O,BrO^5$ | 534·4 | .... | 100·00 | | |

*b. Monobasic.*—Bromic acid and bromate of potash give a yellowish-white precipitate with mercurous nitrate. (Löwig.) The salt is best prepared by precipitating mercurous nitrate in the cold with bromate of potash. The white precipitate, when washed for some time, acquires a yellowish colour, from formation of a small quantity of the salt *a*; a few drops of nitric acid, however, turn it white again. (Rammelsberg.) White powder; crystallizes from the solution in excess of aqueous bromic acid, on evaporation and cooling, in white laminæ. Contains no water. Detonates when heated, but much less strongly than the mercuric salt, and yields metallic mercury. When washed with water, it turns yellowish; and when treated with hot water, it is completely converted into *a*. The solution thereby obtained, which contains mercurous bromate with excess of acid, yields, on evaporation, the salt *b* in laminæ; and the mother-liquid, when further evaporated, gives off bromine, and yields needles of mercuric bromate, because the excess of bromic acid exerts an oxidizing action. The salt dissolves with some difficulty in nitric acid, but easily in hydrochloric acid, with formation of mercuric chloride. (Rammelsberg.)

| | | | | | Rammelsberg. | | |
|---|---|---|---|---|---|---|---|
| | | | | | *Pulverulent.* | | *Laminated.* |
| $Hg^2O$ | 208·0 | .... | 63·72 | ..... | 63·36 | .... | 62·52 |
| $BrO^5$ | 118·4 | .... | 36·28 | | | | |
| $Hg^2O,BrO^5$ | 326·4 | .... | 100·00 | | | | |

F. Bromate of Mercuric Oxide, or Mercuric Bromate.—1. Formed by digesting mercuric oxide with bromine-water, evaporating and dissolving out the mercuric bromide formed at the same time with alcohol, in which the bromate is but very slightly soluble. (Löwig.) 2. By precipitating mercuric nitrate with bromate of potash. (Löwig.) 3. Recently precipitated mercuric oxide immersed in aqueous bromic acid is converted into a white salt, but little of which dissolves in the acid liquid; and that which does dissolve may be recovered by evaporation. (Rammelsberg.) White powder; crystallizes from the boiling aqueous solution in small prisms. (Rammelsberg.) Greyish-white powder. (Löwig.) Detonates sharply even at temperatures between 130° and 140°, the greater part volatilizing in the form of a red vapour consisting of oxygen gas, bromine, dibromide, and protobromide of mercury, and metallic mercury, while a small quantity of mercuric oxide remains behind. The salt is easily decomposed and dissolved by hydrochloric acid. Dissolves slightly in nitric acid, in 650 parts of cold water, and 64 parts of boiling water. (Rammelsberg, *Pogg.* 55, 79.)

| | *Powder.* | | | Rammelsberg. |
|---|---|---|---|---|
| HgO | 108·0 | .... | 44·19 | .... 45·4 |
| $BrO^5$ | 118·4 | .... | 48·44 | .... 45·6 |
| 2HO | 18·0 | .... | 7·37 | .... |
| $HgO,BrO^5 + 2Aq.$ | 244·4 | .... | 100·00 | |

G. Mercuric Phosphobromide.—Phosphuretted hydrogen gas passed through aqueous mercuric bromide, yields a brownish-yellow precipitate, which turns black under water, and is reduced to the state of metallic mercury. (H. Rose.)

H. Mercuric Sulphobromide.—Hydrosulphuric acid gas gives with mercuric bromide the same reactions as with the chloride. An excess of hydrosulphuric acid throws down black protosulphide of mercury; but a smaller quantity precipitates a white compound of the protosulphide with the protobromide. The same compound is obtained by digesting recently precipitated black sulphide of mercury with the aqueous solution of the bromide. After drying, it is yellowish-white. When heated, it is resolved into mercuric bromide and cinnabar. It is blackened by alkalis, but less quickly than the corresponding chlorine compound. It is neither decomposed nor dissolved by nitric acid or oil of vitriol at a boiling heat.

| | | | | H. Rose. |
|---|---|---|---|---|
| 3Hg | 300·0 | ..... | 73·10 | |
| 2S | 32·0 | ..... | 7·80 | ..... 7·89 |
| Br | 78·4 | ..... | 19·10 | |
| 2HgS,HgBr | 410·4 | ..... | 100·00 | |

## Mercury and Chlorine.

A. Dichloride of Mercury, or Mercurous Chloride.—*Subchloride of Mercury, Submuriate of Mercury, Salzsaures Quecksilberoxydul, Versüsster Sublimat, Versüsstes Quecksilber, Mercurius dulcis s. Kalomelanicus s. loticus, Calomel, Draco mitigatus, Aquila mitigata s. alba s. cœlestis, s. Mercurii, Panacea mercurialis s. cœlestis, s. Mercurii, Protochlorure de Mercure.*—Found native in the form of *Horn-quicksilver.*

*Formation.* 1. Mercury slowly absorbs chlorine gas at ordinary temperatures, and produces a grey, pulverulent mixture of mercury and the dichloride; when introduced into chlorine gas at a boiling heat, it burns with a yellowish-red flame, producing dichloride and protochloride of mercury.—2. Mercury, electrified for a considerable time in contact with hydrochloric acid gas, separates the hydrogen, and is itself converted into calomel.—3. Mercury agitated with aqueous sesquichloride of iron, yields calomel and aqueous protochloride of iron; the action is accelerated by the presence of free hydrochloric acid. (Schaffhäutl.)—4. Calomel is likewise formed on bringing mercurous oxide in contact with hydrochloric acid, or a mercurous salt with the chloride of an alkali-metal.—5. On heating a mixture of mercury and the protochloride.

*Preparation.* 1. By triturating 4 pts. (1 At.) of mercuric chloride with 3 pts. (1 At.) of mercury, the mixture being moistened with water or alcohol, and the trituration continued till the mercury has lost its fluidity—then gradually heating the mixture in a glass flask or retort till it sublimes. 4 : 3 is nearly the same ratio as 135·4 : 100. A large portion of the protochloride of mercury is converted into dichloride during the trituration. Trautwein heats the deadened mixture, gently at first, for a few hours, and pulverizes it once more before sublimation.—2. By subliming an intimate mixture of equal parts of mercurous sulphate and common salt:—

$$Hg^2O,SO^3 + NaCl = NaO,SO^3 + Hg^2Cl.$$

Planché (*Ann. Chim.* 66, 168) triturates 8 parts of mercury, 18 parts of dry monobasic mercuric sulphate, and 6 parts of water, till the fluidity of the metal is destroyed, and heats the resulting mercurous sulphate with an equal weight of common salt, till a sublimate is obtained.—3. By deadening 2 At. mercury with 1 At. common salt, and 1 At. peroxide of manganese, and heating the mixture to sublimation with 2 At. oil of vitriol:

$$2Hg + NaCl + MnO^2 + 2SO^3 = NaO,SO^3 + MnO,SO^3 + Hg^2Cl.$$

20 pts. mercury, 8 common salt, 6 peroxide of manganese, and 11 oil of vitriol, yield 16 parts of pure calomel, and 7 parts of calomel mixed with mercury; only a small quantity of corrosive sublimate is formed, and passes over with the watery distillate. (Geiger, *Berl. Jahrb.* 1819, 355; *comp.* Kastner, *Berl. Jahrb.* 1818, 210.)—4. By triturating mercury with common salt, ferric sulphate, and a small quantity of water, till the metal has lost its fluidity, and subjecting the mixture to sublimation. (Schaffhäutl, *Ann. Pharm.* 43, 25.) The basic sulphate of ferric oxide, often occurring as a waste-product, may be made available for this process; a small quantity of ferric chloride may sublime together with the calomel. (Schaffhäutl.) The formula is probably:

$$Fe^2O^3,3SO^3 + 3NaCl + 2Hg = 3(NaO,SO^3) + 2FeCl + Hg^2Cl.$$

The calomel set free in the form of vapour by either of these processes (1—4) is either allowed to collect in the form of a dense, fibrous sublimate, and the product carefully pulverized; or the calomel vapour is cooled under such circumstances that it solidifies in the form of a soft powder instead of a solid cake. This object is attained, according to Jewel and O. Henry (*J. Pharm.* 8, 545; also *Repert.* 15, 115), by causing the calomel vapour to pass into a chamber, into which vapour of water is injected on the other side. According to the new English process, on

the other hand, the calomel, or the ingredients from which it is prepared, is heated in a cast-iron cylinder 2½ feet long, and 1 foot wide, one end of which is provided with an opening serving to introduce and remove the materials, and closed during the operation, while the other end terminates in a contracted neck which opens into the upper part of a brick chamber, 4 feet long and broad, and 6 feet high; in this chamber the calomel condenses in the form of a soft powder. As the iron of the tube decomposes a portion of the calomel, a small quantity of protochloride of mercury is added to the mixture. (Calvert, *N. J. Pharm.* 3, 121.) Soubeiran (*J. Pharm.* 29, 502) adopts the same process, excepting that he heats the materials in an earthen retort, and uses a large earthen vessel as a condensing chamber.—The pulverulent calomel obtained by either of these processes is washed with a large quantity of warm water, or a small quantity of warm alcohol, to free it from the corrosive sublimate with which it is usually contaminated.

5. By precipitating a warm dilute solution of mercurous nitrate with excess of common salt or sal-ammoniac, and washing the precipitate thoroughly with cold water. The calomel obtained by this process, first proposed by Scheele, is in the form of a remarkably fine powder, and has consequently somewhat more active medicinal properties than the ordinary preparation. The more energetic action sometimes produced by this *calomel prepared in the humid way*, may perhaps be due to an admixture of basic mercurous nitrate, or mercuric oxide, which, according to Buchner, Mialhé, and others, are sometimes found in it. This admixture, however, does not occur if the solution of mercurous nitrate be largely diluted, and, if necessary, filtered, before being mixed with the soluble chloride, and if the common salt or sal-ammoniac be added in excess, and the liquid heated for some time in contact with the precipitate.—To the same end, Sefström, Geiger, and Trautwein (*Repert.* 11, 72; 12, 155) recommend that a little nitric acid be added to the mercurous solution before mixing; and Chenevix advises the addition of hydrochloric acid to the solution of common salt. In that case, however, the liquid must not be heated so much, as, otherwise, part of the calomel will be redissolved in the form of protochloride of mercury.—According to Dumas, the calomel obtained by the use of common salt always contains more or less of that substance, and cannot be freed from it by washing; the presence of the salt renders the calomel thus prepared more soluble than that obtained by sublimation; but Mialhé (*J. Pharm.* 22, 586) found only traces of common salt, and no difference in the solubility.—Th. Martius (*Ann. Pharm.* 9, 197) precipitates the dilute mercurous solution with sal-ammoniac, and from the filtrate which contains all the mercuric oxide contained in the solution, he obtains *white precipitate* by the addition of carbonate of soda. The precipitate formed by sal-ammoniac, and washed for a long time with cold water, is free from ammonia. (Fleichmann, *Repert.* 79, 209.)—Guibourt (*J. Pharm.* 15, 315) precipitates the concentrated mercurous solution with hydrochloric acid. [In this last process, the application of heat must be avoided; a dilute solution also is to be preferred.]

*Impurities and Adulterations.* 1. Protochloride of mercury: Cold water or alcohol agitated with the powder for some time and then filtered, turns brown on the addition of hydrosulphuric acid, &c.—2. Basic mercurous nitrates or mercuric oxide: Red fumes evolved on heating the substance in a white flask or tube till it sublimes.—3. Metallic mercury: Grey colour; globules of mercury discernible under

the microscope.—4. Pounded heavy spar and similar impurities remain behind on sublimation.—5. Gum and other organic substances: Empyreumatic odour on the application of heat; solubility in water or alcohol, &c.

*Properties.* The native variety and that obtained by sublimation form crystals belonging to the square prismatic system. The native substance exhibits the forms shown in *Figs.* 25, 29, 30 and 39 (without *p*-faces); the artificial product has the form of *Fig.* 38. In *Fig.* 38, $p:a = 119° 50'$; $p:e = 112° 5'$; $a:q = 150° 10'$; cleavage indistinct, parallel to *q*. (Brooke, *Ann. Phil.* 22, 285).—A totally different crystalline form is given by Schneider (*Kastn. Arch.* 5, 71). In sublimed calomel, the squares prisms are generally united in fibrous masses. Specific gravity of the artificial product, 6·9920 (Karsten); 7·140 (P. Boullay). Softer than calcspar. Dirty white, translucent; acquires a transient yellow colour when heated in the state of powder. The product (5) obtained by precipitation is a white, heavy powder, with a tinge of lemon-yellow.—Calomel volatilizes below a red heat, without previous fusion. According to Faraday (*Pogg.* 19, 552), it does not volatilize at ordinary temperatures.—It is tasteless and inodorous.

| | | | Zaboada. | | Vol. | Sp. gr. |
|---|---|---|---|---|---|---|
| 2Hg | 200·0 | 84·96 | 85 | Vapour of mercury | 1 | 6·9300 |
| Cl | 35·4 | 15·04 | 15 | Chlorine gas | ½ | 1·2271 |
| $Hg^2Cl$ | 235·4 | 100·00 | 100 | Vapour of calomel | 1 | 8·1571 |

| Or: | | Proust. | Chenevix. | Stromeyer. | Zaboada. |
|---|---|---|---|---|---|
| $Hg^2O$ | 208·0 | 88·36 | 86·94 | 88·5 | 88·93 | 89·4 |
| Cl − O | 27·4 | 11·64 | 13·06 | 11·5 | 11·07 | 10·6 |
| | 235·4 | 100·00 | 100·00 | 100·0 | 100·00 | 100·0 |

*Decompositions.*—1. Calomel becomes dark grey by exposure to light [by formation of $Hg^4Cl^2$?].—2. Heated in a current of phosphorus vapour, it yields phosphide of mercury and terchloride of phosphorus. (H. Davy.)—3. When heated with a small quantity of sulphur, it yields cinnabar and mercuric sulphide; with a larger qnantity of sulphur, the products are cinnabar and dichloride of sulphur:

$$Hg^2Cl + S = HgCl + HgS;$$

and, $$Hg^2Cl + 4S = 2HgS + S^2Cl.$$

4. When immersed in cold, aqueous sulphurous acid, it turns grey, and in the same liquid at a boiling heat it becomes greyish-black, from loss of chlorine. In this greyish-black powder, no metallic mercury can be discovered with the lens; but when heated, it is resolved into calomel and metallic mercury; it is probably, therefore, a subchloride. (A. Vogel.)—5. Calomel gives up its chlorine to many of the base metals, both in the dry and in the humid way. On boiling it with copper and water, a green solution is quickly formed, and the copper becomes covered with a black film, from which hydrochloric acid extracts cupric oxide, leaving a residue of metallic mercury. (A. Vogel, *J. pr. Chem.* 8, 107.)—6. By aqueous protochloride of tin, it is reduced to the metallic state, after some time at ordinary temperatures, but quickly on boiling. (A. Vogel, *Kastn. Arch.* 23, 78.) With mineral kermes or *sulphur auratum*, it is gradually converted into black sulphide of mercury and terchloride of antimony. The mixture of calomel with mineral kermes or *sulphur auratum* becomes

grey in the course of 4 weeks, and moist when exposed to the air. Under cold water, the decomposition takes some weeks; in boiling water, it is complete in a few minutes; the water takes up hydrochlorate of antimonic oxide. The decomposition likewise takes place in ether and hot oil of turpentine or oil of lavender, but not in alcohol. (A. Vogel, *Schw.* 33, 291.) Recently precipitated kermes, still moist or dried in the air, turns black in a few minutes when placed in contact with dry calomel; but if it has been dried at 100°, it does not blacken, even when moistened, but only after being several times alternately moistened and heated. Pentasulphide of antimony, recently precipitated and still moist, quickly blackens calomel; if dried in the air, it forms with calomel a yellowish brown mixture, which turns black on the addition of water; after drying at 100°, it acts but feebly even when moistened, unless heat be also applied. (Geiger, *Mag. Pharm.* 29, 240.)—8. Calomel triturated with iodine and water yields protochloride of mercury, which dissolves, and protiodide of mercury, of which the water takes up a small portion. (Planché & Soubeiran, *J. Pharm.* 12, 651; also *N. Tr.* 15, 144.)

$$Hg^2Cl + I = HgCl + HgI.$$

—9. Calomel digested in the aqueous iodides of the alkali-metals, magnesium, zinc, or iron, yields dark green diniodide of mercury and an aqueous metallic chloride. The mercurous iodide thus produced remains unchanged for a long time in the dark; but when exposed to light, it first becomes yellow, and then red from loss of mercury; fuses into a black-brown liquid; gives off mercury and mercuric iodide; and leaves a white residue of chloride of potassium, together with the excess of iodide of potassium employed. (Labouré, *J. Pharm.* 4, 329.)—10. Hot nitric acid dissolves calomel, with evolution of nitric oxide gas, forming a solution of mercuric chloride and mercuric nitrate:

$$3Hg^2Cl + 4NO^5 = 3HgCl + 3(HgO,NO^5) + NO^2.$$

Cold oil of vitriol neither dissolves nor decomposes calomel, even after a long time; but hot oil of vitriol dissolves it (the liquid solidifying in a white saline mass on cooling), giving off sulphurous acid, yielding a sublimate of mercuric chloride, and leaving a residue of mercuric chloride mixed with mercuric sulphate. (A. Vogel.)

$$Hg^2Cl + 2SO^3 = HgCl + HgO,SO^3 + SO^2.$$

11. Calomel immersed in aqueous hydrocyanic acid yields metallic mercury and a liquid which contains cyanide of mercury and hydrochloric acid. (Scheele, *Opusc.* 2, 159.) Part of the calomel remains undecomposed. (Buchner, *Repert.* 9, 303.) The part which remains undissolved is not metallic mercury, but a black powder, which, when heated, gives off calomel vapour, together with a small quantity of permanent gas, and leaves a carbonaceous powder. (Soubeiran, *J. Pharm.* 15, 523.) The resulting liquid always contains sal-ammoniac, even when the hydrocyanic acid used is quite free from ammonia, and therefore, after being precipitated with nitrate of silver, filtered, and evaporated, yields nitrate of ammonia. The black powder which remains undissolved, exhibits, when examined with the microscope, shining points, which, however, do not consist of metallic mercury. It fuses in a glass bulb at 130°, becomes somewhat whiter at 150°, and afterwards exhibits little globules of mercury, which sublime on the application of heat. At a higher temperature, calomel sublimes together with the metallic mercury, and a carbonaceous substance is left behind. Part of the calomel remains undecomposed, even

when an excess of hydrocyanic acid is present. (Deschamps, *J. Pharm.* 25, 22.) The decomposition by hydrocyanic acid must therefore be more complicated than that which would be expressed by the equation:

$$Hg^2Cl + HCy = Hg + HgCy + HCl,$$

and deserves further examination; to the physician, it is important to know that the mild substance calomel, is converted by hydrocyanic acid into a compound which acts so violently as cyanide of mercury.

12. Calomel heated with dry fixed alkalis, yields mercury, oxygen gas, and a chloride of the alkali-metal:

$$Hg^2Cl + KO = KCl + 2Hg + O.$$

By aqueous fixed alkalis it is converted into black mercurous oxide, a chloride of the alkali-metal remaining in solution. Calomel likewise blackens when immersed in aqueous ammonia, not, however, by conversion into mercurous oxide, but into $Hg^2NH^2,Hg^2Cl$. (Kane.) The supernatant ammoniacal liquid contains a small quantity of mercury in solution. (Buchner, *Repert.* 53, 70.) Carbonate of ammonia colours calomel grey and quickly dissolves it, with the exception of a small grey residue of metallic mercury. (Wittstein.) Carbonate of magnesia exerts no action in the cold, even in the presence of water; but at a boiling heat, carbonic acid is evolved, mercury separated, and a solution formed, containing mercuric oxide in combination with magnesia. (Buchner, *Repert.* 3, 31; 4, 289.) ¶ According to A. Vogel, Jun. (*Repert. Pharm.* [3,] 1, 34), calomel heated with water and carbonate of lime (or magnesia), is converted into dinoxide [and protoxide?] of mercury and metallic mercury, carbonic acid being evolved and chloride of calcium formed. The carbonates of baryta and strontia act in a similar manner, but not so strongly. When calomel was boiled with pounded gypsum, chloride of calcium and mercuric sulphate were formed; a similar effect was produced by boiling with sulphate of soda. ¶—13. By aqueous vapour and boiling water, calomel is partly converted into metallic mercury, or into a grey compound of calomel with excess of mercury, and soluble mercuric chloride. When aqueous vapour is passed over calomel powder contained in a glass tube, the water condensed by cooling deposits calomel in a very soft, finely divided state, and is found to contain protochloride of mercury in solution. (Righini, *J. Chim. méd.* 18, 190; also *J. pr. Chem.* 26, 416.) This is also probably the explanation of the fact that whenever calomel is sublimed, a small portion of it is resolved into mercury and corrosive sublimate, and consequently the vapour which rises from it has the power of reddening litmus—an effect which would be produced by corrosive sublimate. In a comparative experiment made by the author, it appeared that the calomel, when sublimed in a current of dry air, was much less decomposed than when the air was loaded with vapour of water. Calomel prepared in the humid way (5) reddens litmus more quickly when sublimed than that which has been prepared by sublimation, probably because it contains more hygroscopic water. (Pagenstecher.) Calomel powder boiled for a long time with large quantities of water frequently renewed, continually diminishes in quantity, and acquires a grey colour, and the water takes up chlorine and mercury. From the contradictory statements made with respect to this reaction, the following facts may perhaps be deduced:—The grey product is basic hydrochlorate of mercurous oxide, which recovers its whiteness by boiling with hydrochloric acid, and when sublimed yields calomel, mercury, and oxygen gas; a small quantity of hydrochloric acid is found in the water. (Donovan.) The grey powder

is basic hydrochlorate of mercurous oxide; the water contains protochlorid of mercury. (Gruner, *Berl. Jahrb.* 1820, 488.) The aqueous decoction yields, on evaporation, a mixture of calomel and corrosive sublimate. (A. Vogel, *Schw.* 33, 291.) The aqueous decoction yields, on evaporation, a small quantity of hydrochloric acid; and leaves a greenish yellow crystalline residue, half soluble in cold, and half in hot water. (Peschiar, *N. Tr.* 5, 2, 33.) When 10 parts of calomel, either sublimed or prepared in the humid way, are boiled in an open vessel with 3000 parts of water, till the quantity is reduced to 1000 parts, the liquid then decanted, and the calomel again boiled with 3000 parts of water down to 1000 parts, there remains from 6·3 to 7·8 parts of *unaltered* calomel, which almost wholly disappears after six similar boilings. The decoction tastes of mercury—does not redden litmus—and gives with hydrosulphuric acid a black, with ammonia or nitrate of silver a white, and with potash a yellowish white precipitate. It covers copper with green basic hydrochlorate of cupric oxide, and does not amalgamate it till hydrochloric acid is added to the liquid. According to this, the decoction should contain basic hydrochlorate of mercuric oxide (or mercuric oxychloride) produced by contact of air. When 1 part of calomel is repeatedly boiled with water, and the whole decoction boiled down to 1 part, the concentrated solution gives a yellow precipitate with potash and white with ammonia: it therefore contains protochloride of mercury. (Simon, *Repert.* 52, 145.) When from 100 to 166 parts of *vapour-calomel* are agitated for an hour with 1667 parts of boiling water in a well-closed bottle and kept at 100°, the water is found to have taken up 0·16 pt. protochloride of mercury; if the air has access to the liquid, a larger quantity of this compound is formed.

14. Boiling hydrochloric acid quickly converts calomel into protochloride of mercury which dissolves, and metallic mercury which remains behind. (Proust, Boullay, *Ann. Chim. Phys.* 34, 343.) On the other hand, when water containing hydrochloric acid is boiled in an open vessel with calomel, the latter is completely dissolved in the form of protochloride, without separation of mercury. (Guibourt, *J. Chim. Méd.* 2, 274.) When 100 parts of calomel are placed in a stoppered bottle, together with 100 parts of hydrochloric acid, and 1667 parts of water thoroughly freed from air by boiling, the liquid, if at the temperature of 40° or 50°, takes up, in the course of 24 hours, 0·67 parts protochloride of mercury; but in an open vessel, it takes up 2·32 parts. (Mialhé.)

15. Calomel sublimed with sal-ammoniac yields mercury and a sublimed compound of sal-ammoniac and protochloride of mercury. (Pettenkofer, *Repert.* 3, 31.) The same decomposition, doubtless induced by the affinity between sal-ammoniac and protochloride of mercury, takes place when calomel is boiled in a solution of sal-ammoniac. (Pettenkofer.) 100 parts of calomel boiled with 200 sal-ammoniac and with water, lose 19 parts; the grey residue contains globules of mercury. (Pfaff, *Schw.* 45, 100.) 100 parts of calomel boiled five times with 100 sal-ammoniac and with water, yield 40 parts of mercury, and a liquid from which alkaline carbonates throw down 60 grammes of white precipitate. (Hennel, *Quart. J. of Sc.* 18, 295.) The sal-ammoniac solution takes up a small quantity of mercuric chloride from the calomel, even at ordinary temperatures. (Mialhé.) A solution of 100 parts sal-ammoniac and 100 common salt in 1667 water, kept for 24 hours at a temperature from 20° to 25° in contact with 100 parts of vapour-calomel, takes up 1 part of mercuric chloride; but at temperatures between 40° and 50°, the quantity of that

compound dissolved amounts to 2·5 parts. The same quantity of mercuric chloride is produced, if the quantity of calomel is only 33 or even 17 parts instead of 100; whence it appears that the quantity of mercuric chloride thus formed depends, not upon that of the calomel, but upon that of the solution of sal-ammoniac and common salt. The concentration of this solution has likewise some influence on the result. When 100 parts of sal-ammoniac and 100 common salt are dissolved in 833 parts of water, and the solution kept in contact for 24 hours at 40° or 50° with 100 parts of calomel, 4 parts of mercuric chloride are dissolved; if the quantity of water amounts to 1667 parts, 3·3 parts of mercuric chloride are dissolved under the same circumstances; with 3333 parts water, 2 parts HgCl; and with 6666 parts water, 1·5 parts HgCl. Access of air likewise influences the quantity of mercuric chloride dissolved. If, under the preceding circumstances, 50 parts of calomel are placed in an open vessel with 100 sal-ammoniac, 100 common salt, and 1637 boiled water, 1·8 part mercuric chloride dissolves in the liquid; whereas in a close vessel only 0·5 part would be formed. Hence it appears that more than two-thirds of the mercuric chloride is produced by the oxidizing action of the air, and one-third by the decomposition of the calomel. Calomel prepared in the humid way likewise yields rather more mercuric chloride than vapour-calomel, a circumstance which accords with its greater activity. (Mialhé, *J. Pharm.* 26, 108; and *N. Ann. Chem. Phys.* 5, 169.) Solution of sal-ammoniac acts upon calomel at ordinary temperatures, and the resulting mercuric chloride may be dissolved out by agitation with ether. A mixture of 3 parts calomel with 20 sal-ammoniac and 20 sugar, kept in paper in a damp place for a week, and then treated with cold water, yields a filtrate from which ether extracts mercuric chloride on agitation. (Larocque, *N. J. Pharm.* 4, 9.) A cold solution of 1 part sal-ammoniac in 1024 water, filtered several times through 96 parts of finely pulverized calomel, yields a filtrate in which no trace of mercury can be detected. (Th. Martius, *Ann. Pharm.* 9, 197.) According to Lepage (*J. Chim. Méd.* 18, 606), a solution of sal-ammoniac, even at temperatures between 38° and 60°, does not take up a trace of mercury from calomel in 24 hours. According to Simon, on the contrary (*Repert.* 52, 145), calomel triturated with sal-ammoniac and a small quantity of water, gives off ammonia, and quickly turns grey, giving up protochloride of mercury to the water. Chloride of potassium, chloride of sodium, and certain other metallic chlorides, act in a similar manner to sal-ammoniac, but not so strongly. (Pettenkofer, Hennel.) Calomel is not decomposed by sublimation with common salt. (Pettenkofer.) To decompose calomel completely with common salt and water, 1 part of calomel must be boiled 10 times in succession with 1 part of common salt and with water. (Hennel.) An aqueous solution of chloride of barium and chloride of calcium, boiled with calomel, dissolves, according to Pettenkofer, only a trace of mercuric chloride; sulphate of potash, nitre, or cream of tartar, none whatever. Even at the ordinary temperature of the air, and at that of the human body, aqueous chloride of potassium or sodium takes a small quantity of mercuric chloride from calomel. When 25 parts of sublimed calomel are placed for several hours in a solution of 100 parts of sal-ammoniac in 833 parts of water, at temperatures between 40° and 50°, 0·75 parts protochloride of mercury is dissolved; the same quantity of chloride of potassium takes up 0·25; and of chloride of sodium or chloride of barium, 0·33 parts of the protochloride. (Mialhé.) When 50 parts of calomel, 100 chloride of potassium or chloride of sodium, and 2083 water, are

placed in a vessel and set aside for 7 days, the liquid being frequently agitated, a filtrate is obtained which turns brown with hydrosulphuric acid; since, however, ether does not dissolve protochloride of mercury from it on agitation, the compound dissolved appears to be, not that substance, but calomel. With the chlorides of barium, calcium, and magnesium, under the same circumstances, a filtrate is obtained which does not turn brown with hydrosulphuric acid. But when the solutions of these same metallic chlorides are boiled, mercury is separated, and the liquid takes up mercuric chloride, which may be dissolved out by ether. If, however, the chloride of potassium or sodium contains a trace of iodide, the calomel turns grey even at ordinary temperatures, and the watery filtrate treated with ether, gives up protochloride together with protiodide of mercury. (Larocque.) According to Wittstein, calomel is soluble for the greater part in sulphate of ammonia, but very sparingly in the nitrate and succinate. Ether does not extract protochloride of mercury from calomel. (Lassaigne, *Ann. Chim. Phys.* 64, 103.)

Calomel forms compounds with anhydrous sulphuric acid, chloride of sulphur, and ammonia.

B. Protochloride of Mercury, or Mercuric Chloride.—*Corrosive Sublimate, Aetzender Quecksilber-sublimat, Aetzsublimat, Sublimat, Muriate of Mercury, Salzsaures Quecksilberoxyd, Mercurius sublimatus corrosivus, Deuto-chlorure de Mercure, Sublimé corrosif.*

*Formation.* 1. When mercury is burned in chlorine gas.—2. In the decomposition of mercuric salts by various metallic chlorides.—3. When mercuric oxide is heated with certain aqueous metallic chlorides. Mercuric oxide boiled with hydrochlorate of magnesia, is dissolved and precipitates the magnesia. (Berzelius, *Jahresber.* 21, 142.) Mercuric oxide boiled in a dilute solution of chloride of calcium, produces no decomposition; but in a concentrated solution, it dissolves, with separation of white flakes of hydrate of lime; but, on the addition of water to the concentrated liquid, chloride of calcium is re-dissolved, and mercuric oxide separated, in combination with a small quantity of mercuric chloride, and mixed with a little carbonate of lime. (Hochstetter, *J. pr. Chem.* 27, 373.) A warm solution of common salt likewise dissolves mercuric oxide, according to Mialhe (*vid. inf.*) and Dranty (*J. Chim. méd.* 12, 651), in the form of mercuric chloride, and the liquid becomes alkaline from the presence of caustic soda.—4. In the decomposition of mercurous oxide, mercurous salts, and of the diniodide, dibromide, and dichloride of mercury by aqueous metallic chlorides. 100 parts of the following mercury-compounds placed in contact for twenty-four hours, at temperatures between 10° and 20°, or 40° and 50°, with 100 parts of common salt and 1667 parts of water, yield the following quantities of mercuric chloride in solution: mercurous oxide at 15°, 1·8 part; at 40°, 3·2 parts of mercuric chloride. (Mercuric oxide at 15°, 7·8 parts; at 40°, 25·7 parts.)—Mercurous iodide at 15°, or at 40°, 0·8 part.—Mercurous bromide at 15°, 1 part; at 40°, 2·5 parts. (If the air be excluded, at least in the beginning, mercuric bromide is dissolved; but if the liquid be exposed to the air, the greater part of that which is dissolved consists of mercuric chloride.)—Mercurous sulphate at 15°, 0·7 part; at 40°, 2·3 parts.—Mercurous nitrate at 15°, 1·2 part; at 40°, 2·3 parts.—Mercurous tartrate at 15°, 1·3 part; at 40°, 1·8 part.—Mercurous acetate at 15°, 0·7 part; at 40°, 1·3 part.—*Mercurius solubilis* at 15°, 2·3 parts; at 40°, 3·7 parts. (Mialhé, *N. Ann. Chim.*

*Phys.* 5, 176.) Again, when mercury is immersed in water containing chloride of ammonium, potassium, or sodium, and the liquid exposed to the air, protochloride of mercury is dissolved, the quantity increasing in proportion as the mercury is more finely divided, and the quantity of metallic chloride in solution is greater. Thus, 100 parts of liquid mercury with 100 common salt, 100 sal-ammoniac, and 1667 water, at 15°, yield 0·7 part protochloride of mercury in 24 hours; but if the mercury has lost its fluidity, the quantity produced at 40° is 1·2 part. Hence may be explained the action of metallic mercury on the human body [?]. (Mialhe, *J. Pharm.* 27, 630; and *N. Ann. Chim. Phys.* 5, 183.)

*Preparation.* 1. By subliming a mixture of equal parts of mercuric sulphate and decrepitated common salt. (*Sch.* 51.) Kunkel.—2. Or: Equal parts of mercuric nitrate, decrepitated common salt, and calcined green vitriol.—3. Or: By triturating 3 parts of mercury with 2 common salt, 2 nitre and 4 calcined green vitriol, till the mercury has lost its fluidity, and then subliming:

$$Hg + NaCl + KO,NO^5 + Fe^2O^3,2SO^3 = HgCl + NaO,SO^3 + KO,SO^3 + NO^4 + Fe^2O^3.$$

In this old Dutch process, the hyponitric acid which escapes is condensed in receivers containing water, and afterwards, under the name of *Sublimate-water*, used for the preparation of mercuric oxide.—4. Or: 10 pts. of mercury, 8 common salt, 6 peroxide of manganese, 11 oil of vitriol, and 3 water. The product is 12·25 parts of corrosive sublimate. (Geiger, *Berl. Jahrb.* 1820, 346):

$$Hg + NaCl + MnO^2 + 2SO^3 = HgCl + NaO,SO^3 + MnO,SO^3.$$

This process had been previously proposed by Fourcroy.—5. By heating mercurous nitrate with hydrochloric acid, till the precipitated calomel is redissolved, and cooling the liquid to the crystallizing point:

$$Hg^2O,NO^5 + 2HCl = 2HgCl + 2HO + NO^4.$$

6. By dissolving mercuric oxide in boiling dilute hydrochloric acid, and repeatedly evaporating and cooling to the crystallizing point.

*Properties.* Crystalline system the right prismatic; *Fig.* 70. Cleavage parallel to $p$, $u$, and $u'$; $u' : u = 93° 44'$; $u' : t = 133° 8'$. (Brooke.)—Sublimed protochloride of mercury exhibits the form of *Fig.* 65; but with $m$-faces (between $u'$ and $u$); also with faces between $i$ and $t$; finally, with faces between $u$ and $m$—$u' : u = 93° 52'$; $u' : t = 133° 4'$; $i : i' = 142° 45'$ [144°?]; $i : t = 108°$; *face between i and t, : face between i′ and t*, backwards $= 111° 38\frac{2}{3}'$; *face between i and t* : $t = 124° 10\frac{2}{3}'$. The crystals obtained by slow evaporation of an alcoholic solution exhibit the form of *Fig.* 71; but the prism is so much shortened, that the upper and lower $y$-faces, which predominate, touch one another. In this form, $u' : u = 86° 12'$ (therefore $u : u'$ backwards $= 93° 48'$); $u : t = 133° 6'$; $y$ above : $y$ below $= 71° 55'$; $t : y = 90°$; $a' : a$ backwards $= 57° 36'$; $a : t = 118° 48'$. (Mitscherlich, *Pogg.* 28, 118.) The crystals obtained by evaporation of the aqueous solution are flat, four-sided prisms, bevelled at the ends with two faces. The translucent cakes of commercial mercuric chloride, obtained by sublimation, exhibit a coarse-grained fracture.—Sp. gr. 5·4032 (Karsten); 5·420 (P. Boullay). White, exhibiting various degrees of translucence, up to transparency. When heated, it fuses, boils, and volatilizes somewhat more readily than calomel. Evaporates even at

ordinary temperatures. (Faraday.) ¶ According to Riegel, however (*Arch. Pharm.* 2nd series, 61, 294), corrosive sublimate does not evaporate at ordinary temperatures, either in the solid state or from concentrated solutions. ¶ The aqueous solution reddens litmus. (v. Bonsdorff.) Has a sharp metallic taste, and is very poisonous.

| | | | | | Vol. | | Sp. gr. |
|---|---|---|---|---|---|---|---|
| Hg | 100·0 | 73·86 | Vapour of mercury | | 1 | | 6·9300 |
| Cl | 35·4 | 26·14 | Chlorine gas | | 1 | | 2·4543 |
| HgCl | 135·4 | 100·00 | Vapour of mercuric chloride | | 1 | | 9·3843 |

| Or: | | | Braamc. & Siqueira. | Proust. | Zaboada. |
|---|---|---|---|---|---|
| HgO | 108·0 | 79·76 | 80·3 | 80·435 | 80·5 |
| Cl—O | 27·4 | 20·24 | 18·6 | 19·565 | 19·5 |
| | 135·4 | 100·00 | 98·9 | 100·000 | 100·0 |

| | Stromeyer. | H. Rose. | Chenevix. |
|---|---|---|---|
| HgO | 80·58 | 81·5 | 82 |
| Cl—O | 19·42 | 18·5 | 18 |
| | 100·00 | 100·0 | 100 |

*Decompositions.* 1. The aqueous solution exposed to sunshine deposits calomel, and gives off oxygen gas and hydrochloric acid. (Boullay, *A. Gehl.* 2, 92; J. Davy.) Hydrochloric acid or sal-ammoniac added to the solution, prevents this decomposition by its affinity for the mercuric chloride. The salt does not suffer decomposition when exposed in the state of powder to sunshine. (J. Davy.)—2. Vapour of phosphorus passed over heated protochloride of mercury yields mercury and terchloride of phosphorus. (H. Davy.) Phosphorus heated with the aqueous solution forms phosphide of mercury, phosphoric acid, and hydrochloric acid. (Boullay.) From the ethereal solution, phosphorus throws down calomel, but no metallic mercury. (Fengler, *Repert.* 9, 259.)—3. Hypophosphorous acid added to the aqueous solution of corrosive sublimate, the latter being in excess, throws down calomel; if the corrosive sublimate is not in excess, metallic mercury is precipitated. (H. Rose, *Pogg.* 9, 375.)—4. Phosphuretted hydrogen gas passed over gently heated protochloride of mercury, causes rapid evolution of hydrochloric acid gas, and forms an orange-yellow sublimate of phosphide of mercury, which, when suddenly heated, is resolved into its elements. (H. Rose.) From the aqueous solution, phosphuretted hydrogen gas throws down yellow phosphochloride of mercury. (H. Rose.)—5. Corrosive sublimate heated with sulphur yields chloride of sulphur and sulphide of mercury. The decomposition may be attended with a violent explosion. (Proust, *Gilb.* 25, 175.)—6. Sulphurous acid added to the aqueous solution, especially when hot, throws down calomel and metallic mercury. At ordinary temperatures, the turbidity does not show itself for 24 hours, but on the application of heat, calomel is immediately precipitated; but to remove the whole of the mercury in the form of calomel, the sulphurous must be added in large excess, and frequently renewed; and the boiling must be repeated several times. The mixture of sulphurous acid and solution of corrosive sublimate gives no precipitate with alkalis, even in excess. (A. Vogel, *J. pr. Chem.* 29, 273.) Sulphite of ammonia has no action on solution of corrosive sublimate [in the cold?] (H. Rose, *Pogg.* 34, 240); but on boiling, it quickly precipitates shining laminæ of calomel, which, when heated for some time with excess of sulphite of ammonia, turn grey, and are afterwards reduced to black

metallic mercury; the reduced metal, heated with hydrochloric acid, unites into globules. (Berthier, *N. Ann. Chim. Phys.* 7, 81,)—7. Hydrosulphuric acid added in excess to the aqueous solution, throws down black protosulphide of mercury; a smaller quantity of hydrosulphuric acid forms a yellow precipitate, which soon turns white. This precipitate is a compound of protochloride of mercury with the protosulphide. (H. Rose.) A similar reaction is produced by alkaline hydrosulphates.

8. Many metals, viz., arsenic, antimony, bismuth, zinc, tin, lead, iron, nickel, and copper decompose protochloride of mercury in the dry way, withdrawing the half or the whole of its chlorine, and separating calomel or metallic mercury, which latter often forms an amalgam with the excess of the other metal. Arsenic forms terchloride of arsenic and a brown sublimate. (Vid. *Arsenio-chloride of Mercury.*) (Capitaine, *J. Pharm.* 25, 549.) An intimate mixture of 3 pts. of antimony and 1 pt. of corrossive sublimate, well pressed into a glass, becomes hot and liquid in the course of half an hour (Olaus Borrichius), and on the application of heat, yields terchloride of antimony and metallic mercury, part of which is apt to pass over in minute globules with the butter of antimony. Any arsenic that may be present passes over in combination with calomel, in the form of a brown powder, which gradually separates from the liquid butter of antimony, and settles at the bottom. (Capitaine.) Tin, heated with corrosive sublimate, forms bichloride of tin, and a grey residue, which contains calomel together with protochloride of tin. (Capitaine.) Silver takes away but half the chlorine; so that calomel sublimes, and chloride of silver remains behind. Many metals likewise reduce the mercury in the humid way. From the aqueous solution, zinc, cadmium, arsenic, and nickel, precipitate the mercury quickly and completely; iron, more slowly; bismuth, lead, and copper, still more slowly; and antimony not at all. Most metals throw down calomel together with the mercury; but zinc, which becomes thoroughly quickened—cadmium, which forms beautiful needles of amalgam—and iron, throw down nothing but metallic mercury. (Fischer, *Pogg.* 9, 258.) Copper immersed in water saturated with corrosive sublimate, precipitates a mixture of calomel and cupric oxide [?], and becomes covered with a fast-adhering black film; strong hydrochloric acid forms therewith a green solution, in which a small quantity of calomel floats, while pure mercury remains upon the copper. If the solution of corrosive sublimate has been previously mixed with hydrochloric acid, only a small quantity of cupric oxide is deposited with the mercury upon the copper; so that the metal, when rubbed, immediately exhibits a silvered surface. The alcoholic and ethereal solutions of corrosive sublimate exhibit similar effects to the aqueous solution. (A. Vogel, *J. pr. Chem.* 8, 107.) Caucal (*J. Chim. Méd.* 5, 358) likewise obtained flakes of calomel, together with mercury, from the aqueous solution. [If the action is long continued, the protochloride of copper is converted into dichloride.] In a solution of 1 pt. corrosive sublimate in 1000 pts. of water mixed with hydrochloric acid, copper immediately becomes covered with a white metallic film; in 5000 parts of water, without the addition of hydrochloric acid, copper exerts no action in the cold, but acquires a golden-yellow colour on boiling; when boiled in a solution to which hydrochloric acid has been added, it turns grey, becoming covered with minute globules of mercury, which may be distinguished by the microscope. These globules are visible by the naked eye, if the quantity of water is greater than from 12,000 to 15,000 parts. (Reinsch, *J. pr. Chem.* 24, 249.) Silver immersed in the

solution of corrosive sublimate throws down calomel, and forms chloride of silver. (A. Vogel.) The chloride of silver thus formed is, however, not the white, but the black variety, which is richer in silver. (Wetzlar, *Schw.* 52, 475.)—9. Arseniuretted hydrogen gas passed through a solution of corrosive sublimate, precipitates a brownish yellow substance ($Hg^3As$, 3HgCl); (H. Rose.)—10. Many metallic sulphides boiled with the aqueous solution of corrosive sublimate are converted into chlorides, and throw down a sulphochloride of mercury, identical with that which would be precipitated by an insufficient quantity of hydrosulphuric acid. Such is the reaction produced by the recently precipitated protosulphides of zinc, cadmium, tin, lead, iron, and copper:

$$2ZnS + 3HgCl = 2ZnCl + 2HgS,HgCl;$$

Similarly, with pentasulphide of antimony:

$$2SbS^5 + 15HgCl = 2SbCl^5 + 5(2HgS,HgCl).$$

Metallic sulphides prepared in the dry way, and likewise native sulphides, act but very slowly on aqueous corrosive sublimate; zinc-blende and native sulphide of antimony exert no perceptible action. (Pagenstecher, *Repert.* 62, 25; 73, 1.) For the decomposition of protochloride of mercury by sulphide of arsenic in the dry way, see *Sulphochloride of Mercury.*

11. Small quantities of protochloride of tin precipitate calomel from the solution of corrosive sublimate; larger quantities separate metallic mercury in the form of a black powder. White flakes of stannic oxide are also formed at the same time [from access of air.] (A. Vogel, *Kastn. Arch.* 23, 79.) Protochloride of tin likewise throws down calomel from the alcoholic solution. (Winckler, *Repert.* 35, 123.) The solution of 1 pt. protochloride of mercury in 500 water becomes blackish grey when mixed with aqueous protochloride of tin; a solution containing 1 pt. in 10,000 or 20,000 acquires a grey colour and gives a precipitate after 24 hours. (Bostock, *Edinb. Med. and Surg. J.* 1825, Jan. 1.) A grey colouring is produced even in 40,000 parts of water. (Geiger, *Mag. Pharm.* 11, 21.)—According to Proust, dichloride of copper dissolved in hydrochloric acid precipitates calomel from solution of corrosive sublimate; Gmelin, on the contrary, obtained nothing but a precipitate of dichloride of copper, easily soluble in hydrochloric acid; arsenious acid also does not throw down calomel.

12. Dry protochloride of mercury heated with caustic fixed alkalis (or alkaline carbonates) yields oxygen gas (and carbonic acid), a sublimate of mercury, and a residue of alkaline chloride. The aqueous solution forms with ammonia a white precipitate of amido-chloride of mercury; with fixed alkalis in excess—and even with the earthy alkalis—it gives a yellow precipitate of mercuric oxide,—or, if the quantity of alkali is insufficient for complete decomposition, a red-brown precipitate of mercuric oxychloride. A perfectly saturated solution of bicarbonate of potash or soda gives with corrosive sublimate a white precipitate which turns reddish in a few minutes, afterwards deep purple-red (Schindler), and consists of red mercuric oxychloride. (Winckler, *Repert.* 36, 250.)—Magnesia likewise throws down mercuric oxide (Geiger, *Mag. Pharm.* 17, 65); if, however, the solution contains an excess of alkaline chloride, it is no longer precipitated by magnesia. (Mialhé, *N. Ann. Chim. Phys.* 5, 178.) Carbonate of magnesia in excess throws down a reddish-yellow precipitate. (Geiger.)—The presence of various organic substances in

the solution of corrosive sublimate interferes with the precipitation, and alters the colour of the precipitate. In presence of strong acetic acid, a solution of corrosive sublimate does not show any white turbidity with potash for a long time; moreover, it retains mercury in solution. (A. Vogel, *J. pr. Chem.* 29, 277.)—In a solution of corrosive sublimate containing a large quantity of sugar or gum-arabic, lime-water produces no precipitate (A. Vogel, *N. Tr.* 3, 2, 559; Sterler, *Repert.* 3, 105); or after some time, a yellowish precipitate which gradually turns black. (Flashof, *N. Tr.* 4, 2, 453; Buchner, *Repert.* 3, 106.)

13. Many organic compounds added to the aqueous solution, especially if aided by light or heat, throw down either mercury or calomel.—Formiate of potash, at temperatures between 50° and 80°, throws down calomel, but after continued boiling it precipitates metallic mercury. (v. Bonsdorff, *Pogg.* 33, 80.) Formiate of soda boiled [for a short time?] with the solution, throws down finely divided calomel, but no metallic mercury. (Döbereiner, *Ann. Pharm.* 3, 142; Winckler, *Jahrb. d. Pharm.* 6, 250.)—Monotartrate of potash and tartar-emetic precipitate calomel, even in the dark, and at ordinary temperatures; the application of heat, however, increases the precipitate. (Brandes, *Ann. Pharm.* 11, 88.)—The solution of corrosive sublimate in hydrated alcohol (not in absolute alcohol or in ether) deposits calomel when exposed to sunshine. Corrosive sublimate immersed in oil of turpentine is not affected by light. (J. Davy, *Phil. Trans.* 1822, 357; also *N. Tr.* 10, 1, 188.) Boullay (*A. Gehl.* 2, 101) had previously obtained calomel with hydrated alcohol.—The solution of corrosive sublimate in water distilled from air-plants, deposits calomel in exposure to light. (Boullay.) Sugar boiled with a solution of corrosive sublimate precipitates calomel. (A. Vogel.)—An aqueous solution of 1 pt. corrosive sublimate in 160 pts. gum-arabic, becomes turbid in a few hours, and in 6 days yields a scanty grey deposit, which blackens by contact with ammonia; a similar effect takes place in a solution of corrosive sublimate mixed with decoction of the yew-tree. One part of corrosive sublimate dissolved in 160 pts. of sarsaparilla decoction, immediately exhibits a strong brown turbidity, and, in the course of 24 hours, the greater part of the corrosive sublimate is precipitated. The precipitate is blackened by ammonia. A similar reaction is exhibited with a solution of *Succus Liquiritiæ* or *Extractum Trifolii fibrini*, excepting that a much larger quantity of sublimate remains in solution. When a mixture of corrosive sublimate is gently ignited with moist charcoal, or with charcoal and oil of lemons, or with oil of lemons alone, or with sugar, or with bread, hydrochloric acid is evolved and metallic mercury separated. Dry charcoal does not reduce the mercury, even when hydrogen gas is passed over the mixture. (Nevins, *Phil. Mag. J.* 13, 431.)

14. Oil of vitriol heated with protochloride of mercury converts but a small portion of it into mercuric sulphate, the greater part volatilizing undecomposed. (A. Vogel, *Schw.* 32, 62; Mohr, *Ann. Pharm.* 31, 183.) According to J. Davy, no decomposition takes place.

15. Protochloride of mercury dissolves in 18·5 parts of water at 14° (J. Davy), and in 2 or 3 parts of boiling water, forming a transparent and colourless solution.—It dissolves in 630 parts of oil of vitriol, and in more than 500 parts of hot nitric acid of specific gravity 1·44. (J. Davy.)—It enters into combination with hydrochloric acid, mercuric oxide, phosphide of mercury, sulphide of mercury, mercuric sulphate, iodide of mercury, amide of mercury, and with ammonia; likewise

with many basic metallic chlorides, forming chlorine-salts—the *Chlorohydrargyrates* of Bonsdorff—in which it plays the part of an acid, and loses its power of reddening litmus.—It dissolves in 3 parts of alcohol, 4 of ether, and abundantly in volatile oils.

C. Mercuric Oxychloride.—1. Formed by boiling protoxide of mercury in solution of corrosive sublimate. (Donovan, Grouvelle.)—1 part of finely powdered mercuric oxide is boiled with a solution of 1 pt. corrosive sublimate for about half an hour, till, in fact, the oxide turns black; as the liquid cools, a small quantity of this compound still separates out. In this reaction, 540 pts. (1 At.) mercuric oxide take up 272·16 (2 At.; 2 . 135·4=270·8) of mercuric chloride, and form 812·16 pts. of oxychloride. When 1 part of mercuric oxide is boiled with 4 parts of corrosive sublimate dissolved in water, the liquid froths up strongly, and the oxide changes colour but slightly even after two hours' boiling. (Kühn, *Schw.* 61, 242.)—When 324 pts. (3 At.) of mercuric oxide obtained by precipitation with potash, are boiled with a solution of 136 pts. (1 At.) of corrosive sublimate, nearly all the latter compound enters into combination with the oxide, so that only 3 parts of oxide can be precipitated from the remaining liquid. The resulting crystalline compound is freed from any uncombined oxide that may be mixed with it, by boiling with a mixture of 50 parts hydrochloric acid and a large quantity of water. (R. Phillips, *Phil. Mag. Ann.* 7, 130.)—2. By gently heating a mixture of 4 [?] At. mercuric oxide with 1 At. corrosive sublimate, or exposing it to the air at ordinary temperatures, till it is converted into a crystalline compound. (Thaulow, *J. pr. Chem.* 31, 370.)—3. By precipitating a solution of corrosive sublimate with a quantity of fixed alkali not sufficient to decompose it completely, and boiling the precipitated oxide for some time with the remaining solution. (Grouvelle, *Ann. Chim. Phys.* 17, 42.)—4. By precipitating a solution of corrosive sublimate at ordinary temperatures with monocarbonate or bicarbonate of potash or soda. (Soubeiran, *J. Pharm.* 16, 662.)—If the alkaline carbonate be added in excess, the resulting precipitate is a red powder, and the liquid contains only traces of mercury; a deficient quantity of alkaline carbonate produces the same red powder at first, but afterwards, small brown crystals, having exactly the same composition, are deposited. If the solution of corrosive sublimate be previously mixed with common salt, so as to produce the less easily decomposible compound of chloride of mercury with chloride of sodium, a white turbidity first makes its appearance, and afterwards the compound gradually separates out entirely in brown crystals. The formation of these crystals may be accelerated by heat, inasmuch as the excess of carbonic acid is then expelled from the alkaline bicarbonate, and its decomposing action on the chloride of mercury thereby prevented; but if the temperature be raised above 40°, the precipitate becomes mixed with variable quantities of free mercuric oxide, and appears more micaceous, and of a deeper red colour. (Soubeiran.)—5. By boiling a solution of corrosive sublimate with carbonate of lime. (Phillips.) Even when the carbonate of lime is in great excess, part of the chloride of mercury remains undecomposed in the solution, in combination with chloride of calcium. Fragments of double refracting spar, immersed for some months in a solution of corrosive sublimate, form closely adhering crystals; pounded marble acts more quickly, and yields distinct crystals. (Phillips.)—6. By passing chlorine gas through hot water in which mercuric oxide is diffused. In this manner, 100 parts of mercuric oxide yield 58 parts

of a violet-brown crystalline powder. The water is found to hold in solution protochloride of mercury and chlorate of mercuric oxide. (Braamcamp & Siqueira.)—The compound may also be formed by mixing hydrate of chlorine with mercuric oxide at ordinary temperatures; hypochlorous acid is then evolved, and the oxide is converted into black, shining spangles. (H. Thaulow, *J. pr. Chem.* 31, 370.)—Chlorine gas passed over gently heated mercuric oxide, produces the oxychloride, with evolution of oxygen and sublimation of a small quantity of mercuric chloride. (Gm.)—7. By precipitating a solution of corrosive sublimate with aqueous chloride of lime.—8. Mercury, immersed in hypochlorous acid gas or its aqueous solution, is converted, without evolution of gas, into an oxychloride (Balard); probably into a mixture of the compound now under consideration with free mercuric chloride:

$$6Hg + 3ClO = HgCl,3HgO + 2HgCl.$$

This compound is likewise sublimed, on boiling a solution of mercuric oxide in nitric acid containing hydrochloric acid. (Paissé, *A. Gehl.* 5, 654.)

Small, brownish black, shining, somewhat transparent crystals, which, according to Phillips, have rhombic faces; or a red-brown powder.

| | | | | | Soubeiran. | | Phillips. | | Thaulow. |
|---|---|---|---|---|---|---|---|---|---|
| 4Hg | 400·0 | .... | 87·07 | .... | 87·50 | .... | 86·58 | .... | 88·79 |
| Cl | 35·4 | .... | 7·71 | .... | 7·12 | .... | 6·85 | .... | 7·68 |
| 3O | 24·0 | .... | 5·22 | .... | | .... | | .... | 3·53 |
| HgCl,3HgO.. | 459·4 | .... | 100·00 | .... | | .... | | .... | 100·00 |

According to Kühn, the compound is: 2HgCl,5HgO; according to Thaulow: HgCl,4HgO; according to Grouvelle: HgCl,5HgO; and according to Phillips: 2HgO,HgCl. Winckler, by precipitating corrosive sublimate with bicarbonate of soda, obtained a precipitate containing 72·58 p. c. HgO, and 24·94 p. c. HgCl.

¶ According to Roucher (*N. Ann. Chim. Phys.* 27, 353; abstr. *Jahresb. L. & K.* 2, 283), the composition of the oxychloride formed by the action of corrosive sublimate on mercuric oxide, is different, accordingly as the red or the yellow modification of the oxide is used in its preparation, and likewise varies with the temperature and the nature of the solvent. At high temperatures, whether the red or yellow variety of the oxide be employed, and whether the chloride be used in the state of aqueous or of alcoholic solution, the products formed are invariably the same, viz., a black insoluble compound, HgCl,2HgO, containing the red oxide, and a white, somewhat soluble substance, consisting of 2HgCl,HgO. —At ordinary temperatures, the yellow oxide always produces the yellow compound HgCl,3HgO. The red oxide, digested in the cold with excess of corrosive sublimate dissolved either in water or in alcohol, forms black HgCl,2HgO; but when the oxide is in excess, and the chloride is used in the state of aqueous solution and frequently renewed, a more energetic action takes place, and the compound formed is HgCl,6HgO + HO; by operating in a similar manner, but using a somewhat larger quantity of the chloride solution at first, the anhydrous compound HgCl,6HgO is produced.—Finally, the nature of the product is influenced by trituration; for, by triturating the red oxide in the cold with solution of corrosive sublimate renewed at short intervals, the product HgCl,4HgO is obtained. ¶

Mercuric oxychloride is resolved, even below a red heat, into oxygen gas, sublimed protochloride of mercury, mixed with a small quantity of calomel, and a residue of mercuric oxide. The liberation of oxygen gas and calomel is produced by the chlorine abstracting a portion of the mercury which is in combination with the oxygen—an effect which takes place to a greater extent, the more suddenly the compound is heated.—100 parts of the compound thus decomposed, yield 20 parts of protochloride of mercury, mixed with a small quantity of calomel, and 80 parts of protoxide (Braamcamp);—according to Proust: 35 per cent. of sublimed protochloride;—according to Grouvelle: from 0·51 to 1·45 per cent. of oxygen gas, 34·93 to 34·35 of a sublimed mixture containing a large quantity of calomel, and a very small quantity of the protochloride, and a residue of 64·56 to 64·20 of oxide.—The proportion of calomel to the protochloride is variable, the latter often predominating. (Soubeiran.)—According to Phillips, the compound, when heated above 106°, gives off a small quantity of water, and afterwards a sublimate consisting, first of protochloride of mercury, then of metallic mercury [probably because the residual oxide was decomposed by the heat] and calomel.—The oxychloride heated to redness with potash, yields oxygen gas, mercury, and chloride of potassium. (Soubeiran.) Aqueous solution of potash separates all the mercury from it in the form of protoxide.—Heated with an acidulated solution of nitrate of silver, it yields chloride of silver. (Soubeiran.)—Heated to 150° in a current of ammoniacal gas, it is converted, with formation of water, into a yellow compound of the oxide, chloride, and amide of mercury. (Ullgren, *Pogg.* 42, 394.)

Mercuric oxychloride dissolves very sparingly in cold water, forming a solution which turns reddened litmus blue. (Guibourt, *J. Chim. méd.* 3, 379.) In boiling water it is somewhat more soluble, and crystallizes from the solution, on cooling, in dark brown, crystalline granules. (Donovan.)

When an aqueous solution of corrosive sublimate is boiled with a small quantity of mercuric oxide, the latter dissolves, as was long ago observed by Proust; the solution becomes turbid on cooling, and deposits mercuric oxychloride.

D. Chloride of Mercury and Hydrogen, or Acid Hydrochlorate of Mercuric Oxide.—135·4 pts. (1 At.) of protochloride of mercury dissolve at 23·3° in 67·7 pts. (1 At.) of hydrochloric acid of specific gravity 1·158, the solution being attended with rise of temperature, and a liquid being formed which has a specific gravity of 2·412, and when cooled a few degrees, immediately solidifies in a pearly mass made up of needles. This substance liquefies when held in the warm hand, and on exposure to the air or on the application of heat, it gives off hydrochloric acid and water, and leaves protochloride of mercury. (J. Davy, *Phil. Trans.* 1822, 361.) The crystals contain 2 At. of chloride of mercury and 1 At. hydrochloric acid. At a higher temperature, 1 At. hydrochloric acid dissolves 4 At. protochloride of mercury, part of which is precipitated on the addition of water. (Boullay, *Ann. Chim. Phys.* 34, 243.)

E. Chlorate of Mercurous Oxide, or Mercurous Chlorate.—Mercurous oxide dissolves at first in aqueous chloric acid, and the salt afterwards separates in greenish yellow granules, having a faint metallic taste. On hot platinum, it deflagrates with a red flame, giving off oxygen gas, and leaving a mixture of protoxide and protochloride of

mercury. It is slightly soluble in boiling water. (Vauquelin, *Ann. Chim.* 95, 103.) ¶ According to Wächter, (*J. pr. Chem.* 30, 321), this salt forms beautiful prismatic crystals, which are soluble in water and alcohol; when heated, it gives off calomel, oxygen, and metallic mercury. Its formula is $Hg^2O,ClO^5$. ¶

F. Chlorate of Mercuric Oxide, or Mercuric Chlorate.—1. Formed by dissolving mercuric oxide in gently heated chloric acid, and cooling the solution to the crystallizing point. (Vauquelin.)—2. By heating mercuric oxide with successive portions of chlorine-water, filtering from the mercuric oxychloride thereby produced, and concentrating the filtrate by evaporation; crystals of corrosive sublimate are then deposited, and chlorate of mercuric oxide remains in solution. (Braamcamp & Siqueira.) Small needles, which redden litmus, taste like corrosive sublimate, and when heated, are resolved into oxygen gas, protochloride of mercury, calomel, and metallic mercury. (Vauquelin.) The salt does not deflagrate on red-hot coals, but sets fire to sulphide of antimony, when mixed with it at ordinary temperatures, and emits sparks when oil of vitriol is poured upon it, the acid at the same time acquiring a yellow colour. Deliquesces in the air. (Braamcamp & Siqueira.)

G. Perchlorate of Mercurous Oxide, or Mercurous Perchlorate.—The solution of mercurous oxide in aqueous perchloric acid, yields, on evaporation, small prisms united in tufts; they are permanent in the air, and deflagrate on red-hot coals. Their solution gives a black precipitate with ammonia. (Serullas.)

H. Perchlorate of Mercuric Oxide, or Mercuric Perchlorate.—Formed by saturating the warm acid with mercuric oxide, which does not neutralize its power of reddening litmus—concentrating the filtrate strongly by evaporation, and leaving it to itself in the drying chamber at a temperature of 25°. In this manner, transparent and colourless crystals are produced, having the form of rectangular prisms and tables. The salt is very deliquescent; its solution yields with potash, a reddish yellow, with ammonia, a white precipitate; and with alcohol, a white precipitate, which aggregates in the form of red mercuric oxide; the liquid filtered from the latter precipitate leaves on evaporation a mixture of mercuric and mercurous salt. (Serullas, *Ann. Chim. Phys.* 46, 306.)

I. Phosphochloride of Mercury.—Formed by passing phosphuretted hydrogen gas through the aqueous or alcoholic solution of protochloride of mercury:

$$6HgCl + PH^3 = Hg^3P,3HgCl + 3HCl.$$

Pure phosphuretted hydrogen gas is completely absorbed; the first bubbles often produce a blackish precipitate, which, however, soon turns yellow. If the air be excluded during the precipitation, and a part of the chloride of mercury be left undecomposed, the liquid will not contain either phosphorous or phosphoric acid, but free hydrochloric acid, which, however, will not dissolve the precipitate. The whole of the mercury is precipitated, provided a sufficient quantity of phosphuretted hydrogen is passed through the liquid; the compound precipitated at the beginning of the action agrees exactly with that which is thrown down towards the end.

The precipitate is quickly washed on the filter with cold water, till the liquid which runs through no longer produces a turbidity in solution of silver; it is then pressed between bibulous paper, dried in vacuo over oil of vitriol, and kept in stoppered bottles completely filled with it.

Yellow powder.—When heated in a retort, it yields a large quantity of hydrochloric acid gas (sometimes mixed with hydrogen gas, with phosphuretted hydrogen, and, especially if the heat be suddenly applied, with vapour of phosphorus), 77·59 per cent. of metallic mercury, and a residue of unfused phosphoric acid. It sometimes also gives off very small quantities of water, but only when it has not been perfectly dried. [Should it not, when dried as completely as possible, and carefully heated, be resolved merely into mercury, hydrochloric acid, and phosphorous acid?

$$Hg^3P + 3HgCl + 3HO = 6Hg + 3HCl + PO^3.]$$

When heated before the blowpipe, it exhibits at first a green phosphoric flame. When washed with water between 60° and 70°, it turns grey from reduction of mercury, and by boiling with water is completely resolved into mercury, and a solution of hydrochloric and phosphorous acids free from mercury. The same decomposition takes place gradually at ordinary temperatures, when the powder is immersed in water or exposed to moist air. A strong solution of potash immediately blackens the yellow powder, and at a boiling heat separates all the mercury in the metallic state, and takes up hydrochloric and phosphorous acid. Hydrosulphuric acid gas passed through water in which the yellow powder is suspended, converts the latter into a black mixture of mercury, sulphide of mercury, and a small quantity of phosphide, which has escaped decomposition by the water; the latter decomposition, however, is the source of the phosphorous acid which, together with the hydrochloric acid, is contained in the watery liquid, The yellow powder heated with dilute nitric acid liberates nitric oxide, and is converted into 86·77 per cent. of calomel; the filtrate contains 9·20 per cent. phosphoric acid, and as much mercury and chlorine as corresponds to 5·41 per cent. of calomel, so that the total quantity of calomel amounts to 92·18 per cent. (H. Rose, *Pogg.* 40, 75.)

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| 6Hg | 600·0 | .... | 78·47 | .... | 78·52 |
| P | 31·4 | .... | 4·11 | .... | 4·04 |
| 3Cl | 106·2 | .... | 13·89 | .... | 13·65 |
| 3HO | 27·0 | .... | 3·53 | .... | |
| $Hg^3P,3HgCl + 3Aq.$ | 764·6 | .... | 100·00 | | |

K. Mercuric Sulphochloride. — 1. Obtained by precipitating a solution of corrosive sublimate with a quantity of sulphuretted hydrogen not sufficient to convert all the mercury into sulphide. The precipitate, which at first is black, brown, or yellow, from excess of mercuric sulphide, soon becomes white, especially on agitation, by taking up a larger quantity of chloride.—2. By precipitating all the mercury from a solution of corrosive sublimate with excess of sulphuretted hydrogen, and boiling the sulphide of mercury, while yet moist, with fresh solution of corrosive sublimate in excess, till it turns white. Black sulphide of mercury previously dried, and likewise cinnabar, undergo no change when boiled with corrosive sublimate. An excess of the black sulphide boiled, while yet moist, with solution of corrosive sublimate, robs the latter of all its mercury.

White powder or friable mass resembling white precipitate.

When slowly heated in a glass tube, it is resolved into mercuric

chloride and cinnabar, both of which sublime, the chloride occupying the upper, and the sulphide the lower place. If a sudden heat be applied, a portion of the undecomposed compound mixes with the sublimed chloride, and remains behind when the latter is dissolved in water. When diffused through water, it is converted by sulphuretted hydrogen into black sulphide of mercury, with separation of hydrochloric acid. In aqueous solution of potash or soda, it turns black and gives up its chlorine, the action being accelerated by heat. The same effect is produced by solution of carbonate of potash or soda, excepting that these reagents act very slowly at ordinary temperatures. The compound heated in a current of chlorine gas yields chloride of sulphur and protochloride of mercury:

$$2HgS,HgCl + 3Cl = 3HgCl + S^2Cl.$$

It is immediately decomposed by boiling nitric acid, the greater part of the sulphur being converted into sulphuric acid. According to H. Rose (*Pogg.* 13, 59) it is not dissolved or decomposed by sulphuric, hydrochloric, or nitric acid, either cold or hot, dilute or concentrated. (*Comp.* Pagenstecher, *Repert.* 73, 1.)

| | | | H. Rose (*mean*). |
|---|---|---|---|
| 3Hg | 300·0 | 81·66 | 81·70 |
| 2S | 32·0 | 8·71 | 8·76 |
| Cl | 35·4 | 9·63 | 9·26 |
| 2HgS,HgCl | 367·4 | 100·00 | 199·72 |

L. Sulphate of Mercurous Chloride.—Calomel (not corrosive sublimate) absorbs the vapour of anhydrous sulphuric acid, and forms therewith a translucent mass. (H. Rose, *Pogg.* 44, 325.)

M. Mercuric Chlorosulphate. — Mercuric sulphate, which is not fusible by itself, forms a fusible compound with protochloride of mercury. (Mohr, *Ann. Pharm.* 31, 183.)

N. Protochloride of Sulphur with Dichloride of Mercury.—*Chlorohyposulfite mercureux.*—1. Formed by very gently heating an intimate mixture of 94 pts. corrosive sublimate and 6 sulphur in a porcelain capsule covered with a funnel, the vessel being from time to time taken off the fire, in order to remove the crystalline film which collects on the surface of the liquid. Only a very small quantity of chloride of sulphur escapes during the process.—2. Calomel powder is mixed with [proto-?] chloride of sulphur to the consistence of a paste, and the mixture placed for 24 hours in a close vessel, after which it is gently heated; the excess of chloride of sulphur escapes first, and subsequently the residue turns red and sublimes.—3. When a mixture of protochloride of mercury and pentasulphide of arsenic is heated in a retort, terchloride of arsenic passes over first, and afterwards mercurous chlorohyposulphite sublimes in very regular crystals, protosulphide of mercury being formed at the same time:

$$7HgCl + AsS^5 = AsCl^3 + 3HgS + 2(Hg^2Cl,SCl).$$

Pale rectangular prisms and needles, sometimes with the longer lateral edges truncated. When heated, they fuse into a brown liquid, which boils and evaporates without decomposition. Water immediately extracts protochloride of mercury from it, separating the sulphur in the form of a granular powder. (Capitaine, *J. Pharm.* 25, 525, and 566; also *J. pr. Chem.* 18, 422.)

| | | | | | Capitaine. |
|---|---|---|---|---|---|
| 2Hg | 200·0 | .... | 69·74 | .... | 69·00 |
| S | 16·0 | .... | 5·58 | .... | 5·65 |
| 2Cl | 70·8 | .... | 24·68 | .... | 24·67 |
| $Hg^2Cl,SCl$ | 286·8 | .... | 100·00 | .... | 99·32 |

O. Mercuric Chloriodide.—HgI, 2HgCl.—Formed by adding protiodide of mercury to a boiling aqueous solution of corrosive sublimate, as long as it dissolves, and leaving the compound to crystallize by cooling. White, indented, fern-like laminæ. The aqueous solution of this compound mixed with sal-ammoniac and carbonate of soda, deposits *white precipitate*, while iodide of sodium remains in solution. (Liebig, *Schw.* 49, 252.)

A solution of corrosive sublimate completely saturated with iodide of mercury deposits, on cooling, nothing but a yellow powder, containing 64·15 pts. (1 At.) of protiodide of mercury, and 35·85 pts. (1 At.) protochloride; this substance soon decomposes spontaneously, assuming the red colour of protiodide of mercury. If, on the other hand, the solution of corrosive sublimate is less completely saturated with iodide of mercury, it deposits, on cooling, first the yellow powder, and afterwards pale yellow crystals, which likewise turn red. (P. Boullay, *Ann. Chim. Phys.* 34, 340.) Larocque (*N. J. Pharm.* 4, 15) occasionally obtained a similar compound, sublimed partly in red crystals, partly in yellow crystals, which soon turned red; these crystals contained chlorine as well as iodine.

A solution of corrosive sublimate saturated in the cold with iodide of mercury, yields, on evaporation and cooling, colourless needles, containing 96·07 parts (40 At.) of corrosive sublimate and 3·93 (1 At.) of mercuric iodide. (Lassaigne.) On adding solution of corrosive sublimate to an aqueous or alcoholic iodine-solution, till the latter is nearly decolorized, and evaporating at a gentle heat, the liquid on cooling deposits white, silky needles, united in feathery tufts, perfectly volatile without decomposition when heated, and containing 97·88 pts. (40 At.) of protochloride of mercury to 2·12 pts. (1 At.) of iodine [doubtless in the form of mercuric iodide; the chlorine liberated from the corrosive sublimate by the iodine probably formed chloride of iodine]. If the iodine is in excess, the needles are reddish, from admixture of mercuric iodide; they may be freed from this impurity by solution in water and filtering. The aqueous solution of the needles gives, in general, the reactions of corrosive sublimate; with ammonia, it yields a yellowish white precipitate, which in time turns brown. The solution gives no blue colour with starch, even on the addition of chlorine or sulphurous acid. (Lassaigne, *Ann. Chim. Phys.* 63, 106; also *J. Chim. Méd.* 13, 11.) [May not Lassaigne's estimation of the iodine be too low, and may not his crystals be identical with those obtained by Liebig?]

## Mercury and Fluorine.

A. Difluoride of Mercury, or Mercurous Fluoride.—This compound sublimes, mixed with calomel, when calomel is heated with fluoride of sodium. White, insoluble in water. It is not produced on subliming protofluoride of mercury with metallic mercury; neither does hydrofluoric acid produce any turbidity in solution of mercurous nitrate; even when the mixture is evaporated over mercury, nothing but the nitrate crystallizes out.

B. Protofluoride of Mercury, or Mercuric Fluoride.—Finely pulverized mercuric oxide forms, with rather strong hydrofluoric acid, a light orange-yellow powder, soluble without colour in a larger quantity of water; with a more dilute acid, the oxide forms at once a colourless solution. From this solution, the mercuric fluoride crystallizes, on evaporation, in dark yellow prisms. (Gay-Lussac & Thénard, Berzelius.) The compound, when heated in a platinum vessel, partly sublimes undecomposed in small, light yellow crystals; but the remaining brown mass contains fluoride of platinum, and forms a brown solution with hydrochloric acid. This solution gives with ammonia a dark brown precipitate, which fumes when ignited, and leaves metallic platinum. When mercuric fluoride is sublimed in glass vessels, almost complete decomposition ensues, gaseous fluoride of silicium being evolved, and mercury set free. The compound forms a white double salt with ammonia. With water, it is resolved into an insoluble yellow basic salt, and a colourless solution of acid *hydrofluate of mercuric oxide*, which has a very sour taste, and, on evaporation, again yields crystals of mercuric fluoride. (Berzelius, *Pogg.* 1, 35.)

C. Mercuric Sulphofluoride. — Formed by passing through the solution of mercuric fluoride in aqueous hydrofluoric acid, a quantity of sulphuretted hydrogen not sufficient to convert all the mercury into sulphide. It may also be obtained by treating the solution of mercuric oxide in hydrofluosilicic acid with sulphuretted hydrogen, but the precipitate then contains a small quantity of silica.

After drying at a gentle heat, it forms a heavy white powder, still containing water; but by long drying at a higher temperature, it is converted into a yellowish-white, anhydrous powder, which turns white again when moistened.

By boiling water it is resolved into soluble fluoride of mercury and insoluble sulphide, mixed, however, with a small quantity of basic hydrofluate of mercuric oxide. When heated in a glass tube, it is converted into gaseous fluoride of silicium [oxygen gas], mercury, and sulphide of mercury. Cold solution of potash turns it red, the hot solution black. With hot oil of vitriol it yields vapour of hydrofluoric acid and the compound of mercuric sulphate with protosulphide of mercury (p. 32). It is not decomposed by hot hydrochloric or nitric acid. (H. Rose, *Pogg.* 13, 66.)

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| 3Hg | 300·0 | .... | 85·55 | .... | |
| 2S | 32·0 | .... | 9·12 | .... | 8·45 |
| F | 18·7 | .... | 5·33 | .... | |
| 2HgS,HgF | 350·7 | .... | 100·00 | | |

In consequence of the difficulty of drying the compound, Rose's estimation of the sulphur turned out too small.

## Mercury and Nitrogen.

A. Nitride of Mercury.—$Hg^3N$.—To form this compound, mercuric oxide precipitated from corrosive sublimate by caustic potash; and then well washed and dried, is placed in a tube, and dry ammoniacal gas passed over it in the cold, till the oxide is completely saturated; the product is then gradually heated to 150° in an oil-bath, the passage of the gas being still continued, as long as water continues to pass off:

$$3HgO + NH^3 = Hg^3N + 3HO.$$

The nitride of mercury thus obtained, is always mixed with globules of mercury, even when it has been heated above 120°. The metallic mercury may be removed by means of cold dilute nitric acid, after which the nitride is to be washed and dried. When ammoniacal gas is passed over mercuric oxide previously heated to a temperature between 100° and 200°, till water is no longer given off, nothing is obtained but a blackish-grey mixture of mercury, mercurous oxide, and a small quantity of nitride of mercury. On treating this mixture with dilute nitric acid, there are obtained, besides metallic mercury, cinnamon-brown curdy flakes, probably consisting of nitride of mercury combined with nitrate of mercurous oxide; when heated, they explode slightly, giving off nitrous fumes, and perhaps also nitrogen gas, and likewise yield metallic mercury and a sublimate of mercurous and mercuric nitrate.

Dark flea-brown powder:

| | | | |
|---|---|---|---|
| 3Hg..... | 300 | .... | 95·54 |
| N..... | 14 | .... | 4·46 |
| $Hg^3N$ ..... | 314 | .... | 100·00 |

This compound deflagrates with a white flame bordered with bluish-purple; the explosion is strong enough to break glass and porcelain, being in fact almost as violent as that of iodide of nitrogen. These effects are produced when the substance is struck with a hammer, or rubbed with a glass rod on a watch-glass, which is then perforated with a round hole. The compound likewise explodes by heat or by contact with oil of vitriol, a white powder remaining in the latter case. To produce the explosion, however, requires a harder blow and a much higher temperature than in the case of iodide of nitrogen. Nitride of mercury carefully and intimately mixed with oxide of copper and heated, yields nitrogen gas and mercury, but no water. Treated in a similar manner with hydrate of potash, it yields ammoniacal gas and sublimed metallic mercury [and oxygen gas?] without detonation. Concentrated nitric acid at 40° dissolves it, forming a solution of nitrate of ammonia and nitrate of mercuric oxide. Dilute sulphuric acid acts upon it at a boiling heat, forming a solution of sulphate of mercuric oxide and ammonia, whilst a small quantity of yellow terbasic mercuric sulphate remains undissolved. Hydrochloric acid forms sal-ammoniac and protochloride of mercury, together with a small quantity of calomel. (Plantamour, *N. Bibl. univers.* 32, 339; also *Ann. Pharm.* 40, 115.)

B. Ammonium-amalgam.—A compound of excess of mercury with ammonium ($NH^4$). Simultaneously discovered by Berzelius and Pontin, and by Seebeck. *Formation.*—1. By electricity.—*a.* By placing strong ammonia in the circuit of the voltaic battery, the negative pole being formed of mercury in contact with the ammonia. (Berzelius & Pontin, *Gilb.* 6, 260; I. 458.)—*b.* By electrifying in a similar manner a cup of carbonate of ammonia (or hydrochlorate: *H. Davy;* or sulphate: *Gay-Lussac & Thénard;* or phosphate) filled with mercury, connected with the negative polar wire, and resting upon a metal plate in connexion with the positive pole. (Seebeck, *A. Gehl.* 5, 482.) Oxygen gas—or chlorine when hydrochlorate of ammonia is used — is evolved at the positive, but scarcely any gas at the negative pole. (I. 460.)—2. By bringing the amalgam of potassium, sodium, or barium in contact with a

moistened ammoniacal salt or its aqueous solution, or with strong aqueous ammonia. (H. Davy, *Phil. Trans.* 1808, 353; 1810, 55; also *Gilb.* 33, 246; 37, 183):

$$x\mathrm{Hg,K} + \mathrm{NH^3,HCl} = x\mathrm{Hg,NH^4} + \mathrm{KCl}.$$

Ammonium-amalgam thus prepared retains a small quantity of potassium or sodium, which renders it more durable. (H. Davy.) Sodium-amalgam acts more powerfully on sal-ammoniac than potassium-amalgam. The best mode of preparation is to heat 1 part of sodium with 100 parts of mercury under rock-oil, till the amalgam forms, set it aside till needles shoot out from it; pour off the portion which still remains liquid; place the needle-shaped amalgam in a watch-glass; and pour upon it a thin stratum of saturated sal-ammoniac (carbonate of ammonia does not act so well). (Böttger, *J. pr. Chem.* 1, 302; 3, 281.)

In all these cases, the mercury swells up to five times its original bulk (Gay-Lussac & Thénard, *Recherches*, 1, 52; also *Gilb.* 35, 133; 36, 217); eight or ten times, according to Davy; twenty times, according to Böttger. When cooled below 0°, the amalgam solidifies, and crystallizes in cubes. (H. Davy.) When cooled to a very low temperature by a vaporizing mixture of solid carbonic acid and ether, it contracts, without giving off gas, and becomes brittle, exhibiting a dark grey, faintly lustrous fracture, and in this state remains undecomposed, but gives off gas as it liquefies. (Grove, *Phil. Mag. J.* 19, 98; also *Pogg.* 49, 210.) At ordinary temperatures, the amalgam has the consistence of butter, and the colour of mercury; it is lighter than water, and when obtained by (1, *a*) exhibits an arborescent, crystalline structure. (Berzelius.)

Ammonium-amalgam, when left to itself, separates spontaneously into liquid mercury, and a mixture of 2 vols. ammoniacal gas and 1 vol. hydrogen.

The amalgam formed by electricity resolves itself into 1 vol. mercury, 4 vols. ammoniacal gas, and 2 vols. hydrogen. (H. Davy.) [This makes, by weight, 17 ammonia and 1 hydrogen to 75333 mercury, or 18 parts (1 At.) ammonium to 75333 (753 At.) mercury.] The amalgam prepared by means of potassium, the volume of which amounts to five times that of the mercury used, yields, on decomposition, 1 vol. mercury to 3·47 hydrogen and 8·67 ammoniacal gas—or, by weight, 1 part nitrogen and hydrogen to 1800 mercury. (Gay-Lussac & Thénard.)

In ammonium-amalgam cooled to a very low temperature by carbonic acid, this decomposition does not take place (Grove); but at −29°, it is as rapid as at ordinary temperatures. (H. Davy.)—The amalgam obtained by the electric method decomposes as soon as it is taken out of the voltaic circuit (Berzelius); that which is prepared with potassium or sodium remains undecomposed for a longer time, because it still retains a portion of these metals. It resists decomposition longest when kept in a vessel filled with hydrogen. (Berzelius.)—The decomposition takes place even under a fixed oil. (H. Davy.) It is accelerated by agitating the amalgam either alone or with mercury, also by contact with rock-oil, and still more with alcohol or ether. (Gay-Lussac & Thénard.)

When the amalgam decomposes in the air, the same phenomena are produced, and are not accompanied by absorption of oxygen or formation of carbonate of ammonia. In water it is resolved into mercury, aqueous ammonia, and hydrogen gas; in oil of vitriol, into mercury, sulphate of ammonia and sulphur. (H. Davy.)

C. Nitrite of Mercurous Oxide, or Mercurous Nitrite.—An aqueous solution of mercurous nitrate absorbs a large quantity of nitrous gas, and forms a solution of mercurous nitrite, while a portion of the nitrite is deposited in the crystalline form. (Peligot, *Ann. Chim. Phys.* 54, 25.)—When, therefore, strong nitric acid is made to act upon mercury in a sealed glass tube, with the view of producing liquid nitric oxide (II. 377), the pressure never rises above two atmospheres. (Niemann, *N. Br. Arch.* 4, 25.)

According to C. G. Mitscherlich, a lemon-yellow, sparingly soluble *basic* salt is obtained by gently heating crystallized mercurous nitrate either alone or over mercury, or by boiling the aqueous solution of that salt with mercury till the liquid acquires a deep yellow colour.

¶ According to Lefort (*N. J. Pharm.* 8, 5), mercurous nitrite is always produced together with the nitrate, and likewise with the nitrite and nitrate of mercuric oxide, when mercury is acted upon by very strong nitric acid. According to Gerhardt, on the contrary, the nitrite of mercurous oxide does not exist, or, at least, has not yet been obtained,—and the salt sometimes described as such is really a nitrate of mercuroso-mercuric oxide. (73.) It has also been stated that mercurous nitrite is formed by the action of hyponitric acid vapour on metallic mercury. Gerhardt, however, finds that the only products of this action are mercurous nitrate and nitric oxide:

$$2NO^4 + 2Hg = Hg^2O,NO^5 + NO^2. \text{ ¶}$$

D. Nitrate of Mercurous Oxide, or Mercurous Nitrate.—*Subnitrate of Mercury.—a. Bibasic.*—1. Formed by washing the sesquibasic or monobasic nitrate repeatedly with cold water, till it has acquired a light lemon-yellow colour. This colour is more quickly produced by boiling the salt with water; care must, however, be taken not to change the liquid too often, and to stop the process as soon as a grey colour (arising from the presence of metallic mercury) begins to make its appearance among the yellow. The addition of potash to the water increases the quantity of bibasic salt, but impairs its colour and renders it less pure. (Kane.)—2. The same salt separates in yellow crystals of the size of needles' heads, when a solution of mercurous nitrate is left to stand for a long time [over mercury]. (Kane.)—The salt, when heated, gives off red vapours and drops of nitric acid [because it contains water], and leaves a residue of mercuric oxide. By long boiling with water, it is converted into a grey powder, consisting principally of globules of mercury, while the water takes up mercuric nitrate. (Kane, *Ann. Chim. Phys.* 72, 252.) The grey powder obtained by treating this salt with a quantity of potash not sufficient to decompose it completely, is not a peculiar basic salt, as Donovan supposes, but a mixture of the yellow salt with mercurous oxide. (Kane.)

| | | | Kane. (1) | Kane. (2) | Donovan. | Marignac. (1) |
|---|---|---|---|---|---|---|
| 4Hg | 400 | 83·51 | 83·12 | 83·28 | 88·6 | 83·42 |
| 2O | 16 | 3·34 | | | | 2·83 |
| $NO^5$ | 54 | 11·27 | | | | 11·69 |
| HO | 9 | 1·88 | | | | 2·06 |
| $2Hg^2O,NO^5 + Aq.$ | 479 | 100·00 | | | | 100·00 |

On boiling the monobasic salt with water till the residue turns grey, and evaporating the filtrate, which contains but a mere trace of mercuric

salt, small, lemon-yellow, shining crystalline scales are produced, containing both dioxide and protoxide of mercury. This salt is perhaps identical with that examined by Kane. (*Vid. sup.*) It decomposes and turns black when boiled with water. Baryta-water converts it into a black powder, which, when treated with hydrochloric acid, yields calomel and a solution of corrosive sublimate; with cold hydrochloric acid, it slowly yields calomel, and then dissolves completely; hot hydrochloric acid dissolves it more quickly.

When the sesquibasic or monobasic nitrate is treated with a smaller quantity of cold water, a white powder is obtained, which, however, on being washed with a fresh quantity of water, is converted into the yellow salt *a*. (Kane.)

¶ *a'*. 5 *At. Base to* 3 *At. Acid ?*—1. Formed by boiling the solution or the mother-liquid of either of the two following salts, *b* or *c*, with excess of mercury for several hours—the water being replaced as it evaporates—and then leaving it to cool;—or by leaving the crystals of *b* or *c* in contact with their mother-liquid and with metallic mercury, at ordinary temperatures. (Marignac, *N. Ann. Chim. Phys.* 37, 328.)—2. By diffusing the monobasic nitrate through a small quantity of water, and heating to the boiling point. (Gerhardt, *Ann. Pharm.* 72, 77.)—3. By heating dilute nitric acid to a temperature between 40° and 80° in contact with mercury.—4. By mixing a solution of the monobasic salt *c* with bicarbonate of potash, till a precipitate is produced, separating the liquid from that precipitate, and leaving it to crystallize by evaporation.—5. By evaporating to dryness the product obtained on treating excess of mercury with strong nitric acid, and digesting the residue in boiling water. (Lefort, *N. J. Pharm.* 8, 5.)—Large, shining, oblique rhombic prisms, belonging to the doubly oblique prismatic system; colourless, or exhibiting a mere tinge of yellow. (Marignac, Gerhardt.)

| | | | Marignac. | Gerhardt. |
|---|---|---|---|---|
| $10Hg$ | 1000 | 81·97 | 81·92 | 81·9 to 82·2 |
| $5O$ | 40 | 3·27 | 3·27 | |
| $3NO^5$ | 162 | 13·28 | 13·11 | |
| $2HO$ | 18 | 1·48 | 1·70 | 2·0 ,, 2·2 |
| $5Hg^2O,3NO^5+2Aq.$ | 1220 | 100·00 | 100·00 | |

Opinions are divided respecting the true formula of this salt. It will be seen that the analytical results obtained by Gerhardt and Marignac agree very closely, and are likewise very near to the numbers calculated from the formula above given. Accordingly, Marignac regards this formula as the true one. Gerhardt, on the contrary, supposes that the crystallized salt is bibasic, ($2Hg^2O,NO^5+Aq.$) identical, indeed, in composition with the yellow powder *a*, which he considers to be merely an amorphous variety of it; in fact, he is of opinion that the determination of the mercury in the preceding analysis is too low, because a perceptible quantity of mercury is always lost in the analysis. This loss Gerhardt estimates at about 1 or 1·5 per cent. in all mercury determinations. If this be admitted, and the per centage of the mercury increased accordingly, the result will be very near to the per centage required by the formula: $2Hg^2O,NO^5+HO$. It must, however, be observed, that such an error would affect the analysis of the yellow powder *a*, as well as that of the crystals; and, nevertheless, Marignac finds in the former a larger per centage of mercury than in the latter. Moreover, the per centage of nitrogen (determined by a process similar to that recommended by Dumas

for the analysis of azotized organic compounds—that is to say, by igniting the salt in a tube, passing the vapour over finely divided metallic copper, and collecting the nitrogen over mercury) is found to be *greater* in the crystals than in the powder—a result which is, of course, independent of any error in the determination of the mercury. On the whole, then, it appears probable that Marignac's formula for the crystallized salt is correct, and that the real bibasic salt is the yellow powder *a*, obtained by treating the sesquibasic or monobasic nitrate with a large quantity of water.—Lefort assigns to these crystals the formula: $2Hg^2O,NO^5+2HO$, differing from that of Gerhardt only in the quantity of water; for the sum of the quantities of water and mercury in the crystals he finds from 85·6 to 85·4 p.c.; Gerhardt's formula requires 85·4.¶

*b. Sesquibasic.*—1. Formed by placing excess of mercury for a considerable time in contact with cold dilute nitric acid, till the crystals of the monobasic salt which form at first, are gradually dissolved and replaced by those of the sesquibasic salt.—2. By heating the monobasic salt with mercurous oxide, and with water mixed with nitric acid. The crystals obtained by (2) have the same composition as those obtained by (1), but a different form, exhibiting therefore a case of dimorphism.* (C. G. Mitscherlich.)—3. By placing 2 pounds of mercury in a flat-bottomed flask, standing on a thick metal plate, so that it may not be over-heated, and covering the mercury with nitric acid of the ordinary commercial strength. In the course of 24 hours, the whole is converted into large crystals of the salt *b*, and a small quantity of mother-liquid. If, instead of the crystals, a warty mass should be obtained, this mass must be dissolved in the smallest possible quantity of water acidulated with nitric acid, and the solution left to evaporate in the hot air chamber. Large crystals then form in the course of two days; they are left to drain upon a funnel, and then washed with a small quantity of nitric acid. (Mialhe, *J. Pharm.* 22, 588.) ¶ 4. The solution of mercury in warm dilute nitric acid, which generally yields the neutral salt, sometimes deposits prismatic crystals of the sesquibasic salt; these, however, when left in the solution for some time, become changed into the neutral salt. (Gerhardt.)—5. By heating the crystals of the normal salt with the mother-liquid from which they have separated, and with excess of mercury, and leaving the solution to crystallize by cooling; this method, however, often yields crystals of the $\frac{5}{3}$-basic salt *a'*. (Marignac.)—6. By boiling 1 pt. nitric acid of specific gravity 1·42 with 5 pts. water and excess of mercury for five or six hours, and replacing the water as it evaporates. If the boiling be not continued long enough, crystals of the salt *b* are deposited. (Lefort.) ¶

Large, transparent, and colourless prisms. The crystals dissolve without decomposition in a small quantity of water; but when treated with a large quantity of water, either cold or hot, they are resolved into the yellow salt *a* and a soluble acid salt. When triturated with common salt and with water, they yield a filtrate free from mercury, and a greenish powder, which may be regarded as a mixture of calomel and mercurous oxide. (C. G. Mitscherlich.)

¶ * This statement respecting the dimorphism of the sesquibasic salt is contradicted by Gerhardt, who suggests that Mitscherlich may have confounded it with the bibasic (or $\frac{5}{3}$-basic) salt *a'*, with which he was not acquainted in the crystalline form. In fact, the process by which Mitscherlich obtained his second modification of the sesquibasic salt is exactly that by which the salt *a'* may be prepared. Moreover, the proportions of mercury in the two salts differ but little.

| | *Crystallized.* | | C. G. Mitscherlich. (1) | (2) |
|---|---|---|---|---|
| $3Hg^2O$ | 624 | 82·22 | 82·09 | 82·83 |
| $2NO^5$ | 108 | 14·23 | 14·21 | 14·19 |
| 3HO | 27 | 3·55 | 3·70 | 2·98 |
| $3Hg^2O,2NO^5+3Aq.$ | 759 | 100·00 | 100·00 | 100·00 |

¶ According to Gerhardt.

| | *Calculation.* | | *Experiment.* |
|---|---|---|---|
| $3Hg^2O$ | 624 | 84·21 | 82·2 to 82·5 |
| $2NO^5$ | 108 | 14·58 | |
| HO | 9 | 1·21 | 1·9 |
| $3Hg^2O,2NO^5+Aq.$ | 741 | 100·00 | |

According to Marignac.

| | *Calculation.* | | *Experiment.* |
|---|---|---|---|
| $4Hg^2O$ | 832 | 82·95 | 82·5 |
| $3NO^5$ | 162 | 16·15 | 4·2 to 4·5 |
| HO | 9 | 0·90 | 1·1 ,, 1·3 |
| $4Hg^2O,3NO^5+Aq.$ | 1003 | 100·00 | |

In determining the formula of this, as of the preceding salt, Gerhardt makes an allowance of about 1·5 per cent. for loss of mercury in the analysis.

Lefort assigns to the sesquibasic salt, the formula $3Hg^2O,2NO^5+2\frac{1}{2}Aq.$; he gives, however, for the sum of the quantities of water and metallic mercury contained in the salt, 82·5 to 82·6 per cent., a result agreeing very nearly with Gerhardt's formula, which requires 80·9 per cent. Hg + 1·3 Aq. = 82·2. ¶ Kane regards the crystals as a compound of the salts *a* and *c*. = $(2Hg^2O,NO^5+Aq.)+Hg^2O,NO^5+2Aq.$

*c. Monobasic.*—Formed by placing excess of mercury in contact with cold dilute nitric acid, till short prisms are produced. These, if left in the solution for a long time, are converted into the larger crystals of the salt *b*. (C. G. Mitscherlich.)—2. By dissolving mercury in moderately strong nitric acid; evaporating the solution, which likewise contains mercuric salt, to dryness; triturating the residue with mercury and water in a warm mortar, till the fluidity of the metal is destroyed; then dissolving in hot water slightly acidulated with nitric acid; filtering, and cooling the liquid to the crystallizing point. (Bucholz.) Short, transparent, and colourless prisms. (C. G. Mitscherlich.) ¶ Rhombic tables derived from an oblique prism with rhombic base, belonging to the oblique prismatic system. The first crystalline deposit often consists of right prisms of the salt *b*; but these, when left for some time in the acid mother-liquid, are converted into the rhombic tables of the neutral salt. The lateral edges of these crystals are sometimes replaced by broad faces, whereby they are converted into six-sided prisms. (Gerhardt.) ¶

| | *Crystallized.* | | C. G. Mitscherlich. |
|---|---|---|---|
| $Hg^2O$ | 208 | 74·29 | 73·78 |
| $NO^5$ | 54 | 19·29 | 19·57 |
| 2HO | 18 | 6·42 | 6·65 |
| $Hg^2O,NO^5+2Aq.$ | 280 | 100·00 | 100·00 |

Lefort assigns to this salt the formula: $2Hg^2O,HO,NO^5+NO^5,4\frac{1}{2}HO.$

The salt, when heated, is resolved into hyponitric acid vapour and a residue of mercuric oxide:

$$Hg^2O,NO^5 = 2HgO + NO^4.$$

When thrown on red-hot coals, it detonates slightly, but with a bright flame. Mixed with phosphorus, it detonates violently when struck with a hot hammer. (Brugnatelli, *Ann. Chim.* 27, 74.) When it is triturated with common salt, and the mixture exhausted with water, the filtrate contains neither mercury nor free acid, and the residue on the filter consists of pure white calomel. (C. G. Mitscherlich.) It dissolves completely in a small quantity of warm water. When treated with a larger quantity of water, it is resolved into a soluble acid salt and the insoluble salt *b*, which, by a still larger quantity of water is converted into the salt *a*, and then further decomposed. According to Proust, the insoluble residue produced by the action of hot water amounts to 36 or 37 per cent.; according to Grouvelle, cold water leaves a residue of 15·3 per cent. In water containing a small quantity of nitric acid, the monobasic salt dissolves completely, yielding a solution of the acid salt *c*.

*d. Acid Mercurous Nitrate.—Solutio Mercurii frigide parata.*—1. Formed by dissolving the salt *b* or *c* in warm water, acidulated with a small quantity of nitric acid.—2. By leaving excess of mercury for several months in contact with very dilute nitric acid.—3. By boiling excess of mercury with very dilute nitric acid. The solution prepared by this method is more likely to contain mercuric salt.—4. By dissolving mercury in hot concentrated nitric acid, evaporating to dryness, triturating the residue with excess of mercury till the fluidity of the latter is destroyed, and dissolving in warm water slightly acidulated with nitric acid. (Bucholz.) Colourless liquid, which deposits crystals of the salt *c* in the cold. The skin wetted with the solution and exposed to light, acquires a purple stain, which afterwards turns black. The solution of this salt, when exposed to the air, takes up oxygen and is converted into mercuric nitrate; the same change is produced by continued boiling, mercury being then given off together with the water. (Proust.) With hydrocyanic acid, it yields a precipitate of metallic mercury (Scheele, *Opusc.* 2, 165), cyanide of mercury being formed at the same time. (Fr. John, *Ann. Pharm.* 21, 149.) The supernatant liquid contains cyanide of mercury, nitrate of ammonia, and carbonic acid. (Deschamps, *J. Pharm.* 25, 22.) The decomposition probably takes place according to the following formula:

$$6Hg^2O,NO^5 + 5C^2NH = 8Hg + 4(Hg,C^2N) + NH^3NO^5 + 5NO^5 + 2CO^2 + 2HO.$$

The formula given by Deschamps is not correct. (For the other reactions of the solution of mercurous nitrate, vid. *Mercurous Salts*, pp. 6, 7.)

¶ D′. Mercuroso-mercuric Nitrate.—When a solution of mercurous nitrate is evaporated in a basin, the edges of the vessel, where the heat is the greatest, become covered with a light yellow salt, the formula of which is $Hg^2O,NO^5 + 2HgO$. (Gerhardt.) A salt having the same composition had previously been analyzed by Brooke. The same compound is formed, with evolution of nitric oxide, when monobasic mercurous nitrate is fused. This is the salt which Lefort and C. G. Mitscherlich regard as mercurous nitrite; it cannot, however, contain nitrous acid, because when treated with strong oil of vitriol, it evolves nothing but nitric acid, and, moreover, hydrochloric acid converts it into the insoluble dichloride and soluble protochloride of mercury. (Gerhardt.) ¶

E. Nitrate of Mercuric Oxide, or Mercuric Nitrate. — *a. Sexbasic.*—Formed by boiling the yellow salt *b* with water. The nitric acid is not completely removed, even by several hours' boiling, but it gradually diminishes in quantity. (Kane.) According to Murray, also, long boiling with water does not separate pure mercuric oxide, but according to C. G. Mitscherlich it does. Brugnatelli had previously recommended the boiling of mercuric nitrate with water as a means of obtaining the oxide; but the process is costly and uncertain, and Döbereiner, who tried it, obtained but a very small product.—The sexbasic nitrate is a brick-red powder which, when heated, gives off red vapours together with a trace of water, and leaves pure mercuric oxide. (Kane, *Ann. Chim. Phys.* 72, 236.)

| | | | Kane. | Grouvelle. |
|---|---|---|---|---|
| 6Hg | 600 | 85·47 | 86·17 | 88·97 |
| 6O | 48 | 6·84 | | |
| $NO^5$ | 54 | 7·69 | | 11·03 |
| $6HgO,NO^5$ | 702 | 100·00 | | 100·00 |

Grouvelle treated his salt (which was probably the quadrobasic nitrate, and which Kane regards as a mixture of *a* and *b*) with boiling water for a short time only; when boiled for a longer time, it gives off acid, and, according to the same authority, turns red-brown.

*b. Terbasic.*—Remains behind when the crystallized bibasic salt is washed with cold water, as long as the water acquires an acid reaction.—Heavy yellow powder.—Cold water exerts no further action; boiling water dissolves out the monobasic nitrate and leaves the salt. *a.* (Kane.)

| | | | Kane. |
|---|---|---|---|
| 3Hg | 300 | 77·52 | 76·4 to 78·31 |
| 3O | 24 | 6·20 | |
| $NO^5$ | 54 | 13·95 | |
| HO | 9 | 2·33 | |
| $3HgO,NO^5 + Aq.$ | 387 | 100·00 | |

*c. Bibasic.*—The acid solution *d*, when cooled and evaporated, yields this salt in long prisms and needles, which are transparent and colourless, and, according to Kane, have a metallic, non-acid taste. The crystals, when heated, resolve themselves into aqueous nitric acid partly decomposed, and mercuric oxide. The crystals triturated with common salt and afterwards with water, yield protochloride of mercury in the filtrate, and a red powder [mercuric oxychloride] on the filter. (C. G. Mitscherlich.) With cold water, they are resolved into the yellow terbasic, and the soluble monobasic salt:

$$2(2HgO,NO^5) = 3HgO,NO^5 + HgO,NO^5.$$

The aqueous solution thereby obtained again yields crystals of the salt *c*, on evaporation and cooling. 100 parts of the crystals treated with water, yield 26 parts of the basic salt. (Grouvelle.) The crystals deliquesce in moist air. (Donovan, Kane.) They dissolve completely in water acidulated with nitric acid, forming a solution of the following compound.

| | *Crystallized.* | | C. G. Mitscherlich. |
|---|---|---|---|
| 2HgO | 216 | 75·00 | 75·88 |
| $NO^5$ | 54 | 18·75 | 18·90 |
| 2HO | 18 | 6·25 | 5·22 |
| $2HgO,NO^5 + 2Aq.$ | 288 | 100·00 | 100·00 |

*d. Monobasic?—Solutio Mercurii calide parata.*—1. By dissolving mercuric oxide in nitric acid.—2. By dissolving mercury in excess of hot strong nitric acid, and boiling till a sample diluted with water is no longer rendered turbid by a solution of common salt.—3. By boiling mercurous nitrate (*a* to *c*) with excess of nitric acid, and continuing the boiling till a diluted sample no longer gives a precipitate of calomel with excess of common salt. The solution concentrated as much as possible by evaporation, is somewhat viscid, and, according to Proust, has a specific gravity of 3·47; it has a sharp metallic taste, and when aided by light, imparts a blackish red stain to the skin. On further evaporation (which causes an escape of acid) and cooling, it yields crystals of the bibasic salt. Also, when aqueous protochloride of mercury is precipitated by an equivalent quantity of nitrate of silver, and the filtrate, which must contain the monobasic nitrate of mercuric oxide, is evaporated, the bibasic salt still crystallizes out. (C. G. Mitscherlich.)—Water added to the concentrated solution throws down the yellow terbasic salt; the dilute solution richer in acid, is no longer precipitated by a further addition of water.—Protochloride of tin throws down calomel from the solution. (Zaboada.) The solution easily takes up diniodide, dibromide, and dichloride of mercury; and from these solutions, the mercury of the three compounds just mentioned may be precipitated in the form of calomel by common salt, but only when that substance is added in sufficient excess to convert the whole of the mercuric nitrate into corrosive sublimate. The iodide, bromide, chloride, cyanide, and sulphocyanide of silver likewise dissolve in the solution of mercuric nitrate. (Wackenroder, *Ann. Pharm.* 41, 317.)

¶ E′. Phosphonitrate of Mercurous Oxide, or Mercurous Phosphonitrate.—When a solution of ordinary phosphate of soda is poured into excess of mercurous nitrate dissolved in nitric acid, a white or slightly yellowish precipitate is formed, which disappears at first, but afterwards becomes permanent, and quickly settles down; when examined by the microscope, it is found to consist of prismatic laminæ. It may be washed with cold water. (Gerhardt, *Ann. Pharm.* 72, 81.)

| | | | Gerhardt. |
|---|---|---|---|
| $4Hg^2O$ | 832·0 | 85·29 | 84·9 |
| $NO^5$ | 54·9 | 5·55 | 5·8 |
| $PO^5$ | 71·4 | 7·32 | 8·6 |
| 2HO | 18·0 | 1·84 | 2·2 |
| $Hg^2O,NO^5+3Hg^2O,PO^5+2Aq.$ | 975·4 | 100·00 | 101·5 |

When, on the contrary, the mercurous nitrate is poured into excess of phosphate of soda, the precipitate is quite destitute of crystalline character, and has exactly the composition of terbasic mercurous phosphate. Gerhardt.) ¶

F. Nitrate of Mercurous Oxide with Phosphide of Mercury.—Phosphuretted hydrogen gas passed through a solution of mercurous phosphate, yields a deep black precipitate. This precipitate must be washed as quickly as possible with cold water, and dried in vacuo over oil of vitriol; but however quickly this may be done, globules of mercury, according to Rose, are sure to separate out, because a portion of the dioxide of mercury resolves itself into metallic mercury and protoxide; probably, also, because there does not exist such a compound as $Hg^6P$.

The precipitate, which probably consists of phosphide of mercury, nitrate of mercurous oxide, and water, crackles violently when heated, and after ignition leaves a residue of phosphoric acid. (H. Rose.)

G. Nitrate of Mercuric Oxide with Phosphide of Mercury.—Formed by passing phosphuretted hydrogen gas through a dilute solution of acid mercuric nitrate. The first bubbles produce a yellowish precipitate, which, however, soon turns white. The precipitate is collected on a filter, washed with cold water, and dried in vacuo. After drying, it is yellow, but on exposure to the air takes up water, and becomes white again. Detonates violently when gently heated (a piece of the size of a pea making a noise like a pistol-shot), less violently by percussion; it likewise explodes in chlorine gas, probably on account of the heat developed. When chlorine gas is passed through water in which the compound is diffused, it is decomposed, and dissolves quietly. (H. Rose, *Pogg.* 40, 75.)

| | | | | H. Rose. |
|---|---|---|---|---|
| 9Hg | 900·0 | 78·85 | | 78·89 to 79·69. |
| 6O | 48·0 | 4·21 | | |
| P | 31·4 | 2·75 | | 2·95 |
| $3NO^5$ | 162·0 | 14·19 | | |
| $Hg^3P + 3(2HgO,NO^5)$ | 1141·4 | 100·00 | | |

H. Nitrate of Mercuric Oxide with Sulphide of Mercury.—Formed by passing sulphuretted hydrogen, in less than equivalent quantity, through a solution of mercuric nitrate, washing with cold water (taking care not to wash too long), and drying. If the washing be too long continued, the precipitate acquires a yellowish colour, from incipient decomposition. The white precipitate heated in a glass tube yields nitrous fumes, sulphuric acid, a large quantity of mercury, and a small quantity of mercuric sulphide. When suspended in water through which sulphuretted hydrogen gas is passed, it is completely resolved into sulphide of mercury and aqueous nitric acid. In cold aqueous solution of carbonate of potash or soda, it gradually turns yellow, and afterwards black; a boiling solution immediately turns it black. Dissolves in hot aqua-regia, with decomposition, and formation of sulphuric acid. (H. Rose, *Pogg.* 13, 67:)

| | | | | H. Rose. |
|---|---|---|---|---|
| 3Hg | 300 | 76·14 | | 76·35 |
| O | 8 | 2·03 | | |
| 2S | 32 | 8·12 | | 7·78 |
| $NO^5$ | 54 | 13·71 | | 12·80 |
| $2HgS + HgO,NO^5$ | 394 | 100·00 | | |

I. Nitrate of Mercuric Oxide with Iodide of Mercury.—1. Formed by mixing a boiling solution of mercuric nitrate with iodide of potassium, filtering, evaporating, and cooling to the crystallizing point. (Liebig, *Schw.* 49, 255.)—2. By adding excess of iodine to a solution of mercuric nitrate of sp. gr. 1·35, and mixed with a sufficient quantity of free nitric acid, to prevent turbidity on the addition of water. On cooling, the liquid solidifies in a crystalline mass, having a pearly lustre. (Preuss.)—3. By dissolving protiodide of mercury in a solution of mercuric nitrate, and leaving the compound to crystallize by cooling. (Preuss, *Ann. Pharm.* 29, 326.)—4. By dissolving diniodide of mercury (or protiodide, half the

iodine then escaping) in hot nitric acid, whereby nitric oxide is evolved, and leaving the solution to cool. (Souville, *J. Pharm.* 26, 474.)

$$3Hg^2I + 4NO^5 = 3(HgI + HgO,NO^5) + NO^2.$$

The crystals must be merely pressed between bibulous paper, as they would be decomposed by washing with water or alcohol.

White pearly scales and needles. (Preuss, Souville.) Liebig obtained red scales. [Perhaps they were coloured by admixture of free mercuric iodide.] The compound, heated in a glass tube, fuses, gives off nitrous fumes, a sublimate of mercuric iodide, and a residue of mercuric oxide. Aqueous ammonia or potash separates mercuric oxide from it, and forms a compound of iodide of mercury with iodide of ammonium or potassium. (Preuss.) Water decomposes it completely into mercuric iodide and soluble mercuric nitrate. If the water be acidulated with nitric acid, so that no basic nitrate of mercuric oxide shall remain mixed with the iodide, 100 parts of the compound will yield 64 parts of mercuric iodide, and a solution, which, when treated with sulphuretted hydrogen, gives 30·33 pts. sulphide of mercury [and therefore contains 28·24 mercuric oxide]. (Preuss.) The compound is likewise decomposed by alcohol, even of the strength of 40° Bm. (Souville.)

*Calculation*, according to Souville.

| | $HgI + HgO,NO^5$. | | |
|---|---|---|---|
| HgI | 226 | .... | 58·25 |
| HgO | 108 | .... | 27·83 |
| $NO^5$ | 54 | .... | 13·92 |
| | 388 | .... | 100·00 |

*Calculation*, according to Preuss.

| | $2HgI + 2HgO,NO^5$. | | |
|---|---|---|---|
| 2HgI | 452 | 62·60 | .... 64·00 |
| 2HgO | .... 216 | 29·92 | .... 30·33 |
| $NO^5$ | 54 | 7·48 | .... |
| | 722 | | .... 100·00 |

Preuss also supposes that the compound contains two atoms of water; but this is inadmissible, according to his own analysis.

K. Mercurate of Ammonia.—Formed by digesting mercuric oxide with aqueous ammonia at a gentle heat. (Proust.) Mercuric oxide precipitated from solution of corrosive sublimate by potash, and then washed and dried, may be used for this purpose; the ammonia may be left to act upon it for some days in the cold, or it may be heated to the boiling point. (Kane, *Pogg.* 42, 383; also *Ann. Pharm.* 42, 383.) 108 parts of the oxide increase in weight by 14·7 parts, in consequence of taking up the ammonia. (Guibourt.)

Light yellow powder (Proust, Plantamour); yellowish white (Kane); acquires a brown-red colour when heated. (Kane.) Detonates on red-hot coals, but less strongly than fulminating gold. (Proust, Kane.) When carefully heated in a tube, it gives off a large quantity of ammonia, nitrogen gas, and water, subsequently oxygen gas and vapour of mercury. As long as the compound is not completely decomposed, the mass appears brown-red while hot, and becomes yellowish white again on cooling. (Kane.) When mercuric oxide is digested in ammonia, a small portion of mercury dissolves; the white mercurate of ammonia produced dissolves quickly in warm hydrochloric acid; perfectly, also, in a large quantity of warm aqueous carbonate of ammonia. (Wittstein, *Repert.* 57, 48.)

| | | | | | Kane. |
|---|---|---|---|---|---|
| $NH^3$ | 17 | .... | 4·74 | .... | 4·10 |
| 3Hg | 300 | .... | 83·57 | .... | 83·68 |
| 3O | 24 | .... | 6·68 | .... | 6·60 |
| 2HO | 18 | .... | 5·01 | .... | 5·62 |
| $NH^3,3HgO + 2Aq.$ | 359 | .... | 100·00 | .... | 100·00 |

When dry ammoniacal gas is passed over yellow mercurate of ammonia at 150°, the latter is converted into a cinnamon-coloured powder, which, when heated upon platinum-foil, spreads itself over the platinum, gives off water and ammonia, and is transformed into red oxide of mercury. Mixed with nitric acid, and evaporated to dryness, it gives off a small quantity of gas, and yields a white, insoluble powder, which comports itself like Kane's compound: $Hg,NH^2 + 3HgO,2NO^5$. (Plantamour, *N. Bibl. univers.* 32, 339; also *Ann. Pharm.* 40, 120.)

¶ According to Millon (*Compt. rend.* 21, 826), the compound formed by the action of ammonia on mercuric oxide is an oxy-amide of mercury, the composition of which may be expressed by the formula:

$$3HgO,HgNH^2,HO + 2Aq.$$

In vacuo over sulphuric acid, it loses 2 At. water, turns brown, and in that state undergoes no alteration by exposure to the air at ordinary temperatures; at a temperature between 100° and 130°, it gives off a third atom of water. The yellow hydrated compound absorbs carbonic acid from the air, and turns white. The properties of this compound are those of a strong base; it expels ammonia from its salts. A dilute solution of potash has no action upon it; indeed, it is decomposed only by very strong potash, and at a boiling heat. The dry brown compound is resolved by fusion with hydrate of potash into nitrogen, metallic mercury, and mercuric oxide [what becomes of the hydrogen?]. It combines in definite proportions with carbonic acid, nitric, sulphuric, and oxalic acid, forming salts whose composition may be thus represented:

| | |
|---|---|
| The anhydrous base | $3HgO,HgNH^2$ |
| The base dried over oil of vitriol | ,, ,, $+HO$ |
| The hydrated base | ,, ,, $+HO+2Aq.$ |
| Carbonate dried at 135° | ,, ,, $+CO^2$ |
| Hydrated carbonate | ,, ,, $+CO^2+Aq.$ |
| Oxalate | ,, ,, $+C^3O^3$ |
| Sulphate | ,, ,, $+SO^3$ |
| Nitrate | ,, ,, $+NO^5+Aq.$ |
| Bromate | ,, ,, $+BrO^3$ |
| Chloride | $2HgO,HgCl,HgNH^2$ |
| Iodide | $2HgO,HgI,HgNH^2$ ¶ |

L. Hyposulphite of Mercuric Oxide and Ammonia. — First obtained by Kirchhoff. Finely divided mercuric oxide dissolves in warm, moderately concentrated solution of hyposulphite of ammonia, without causing an evolution of heat. Alcohol added to the solution separates the salt in colourless prisms, which decompose so easily that the mere act of collecting them causes a separation of cinnabar [and formation of sulphuric acid?]; when exposed to light, they quickly turn grey. Their aqueous solution deposits black sulphide of mercury on boiling, and generally cinnabar, when left to stand quietly. (Rammelsberg, *Pogg.* 56, 318.)

| | *Crystallized.* | | Rammelsberg. | | |
|---|---|---|---|---|---|
| $4NH^3$ | 68 | .... | 14·47 | .... | 14·14 |
| $HgO$ | 108 | .... | 22·98 | .... | 23·94 |
| $5S^2O^2$ | 240 | .... | 51·06 | .... | |
| $6HO$ | 54 | .... | 11·49 | .... | |
| $4(NH^4O,S^2O^2) + HgO,S^2O^2 + 2Aq.$ | 470 | .... | 100·00 | | |

M. *Trisulphate of Mercurous Oxide* with *Mercurous Amide?*—Monosulphate of mercurous oxide, when treated with aqueous ammonia, is

converted into a dark grey powder, which appears to be: $3\,Hg^2O,SO^3 + Hg^2NH^2$. In this reaction, 992 parts (4 At.) of mercurous sulphate yield at most 116·6 parts (nearly 3 At.) of sulphuric acid to the liquid, and the grey powder produced amounts to at least 823·7 parts (nearly 1 At.):

$$4(Hg^2O,SO^3) + 4NH^3 = (Hg^2,NH^2 + 3Hg^2O,SO^3) + (3NH^3,SO^3) + HO.$$

The grey powder, when heated, gives off water, ammonia, sulphurous acid, oxygen gas, and mercury. The ammonia produced by this decomposition never exceeds 3 per cent. (Kane, *Ann. Chim. Phys.* 72, 283.)

| | *Calculation*, | according to Kane. | |
|---|---|---|---|
| $2Hg$ | 200 | .... | 22·73 |
| $NH^2$ | 16 | .... | 1·82 |
| $3Hg^2O$ | 624 | .... | 70·91 |
| $SO^3$ | 40 | .... | 4·54 |
| | 880 | .... | 100·00 |

N. Trisulphate of Mercuric Oxide with Mercuric Amide.—*Ammoniacal Turpethum.*—First obtained by Fourcroy; its true composition was afterwards ascertained by Kane.—1. Formed by treating monosulphate of mercuric oxide with aqueous ammonia. Yellow trisulphate of mercuric oxide is first produced, but the whole is gradually converted into a white powder; a boiling heat accelerates the process, but does not alter the product. 592 parts (4 At.) of mercuric sulphate give up 119·8 parts (3 At.) of sulphuric acid to the boiling ammonia, and yield 469·5 parts (nearly 1 At.) of ammoniacal turpethum. (Kane.) On slowly evaporating the ammoniacal solution, or mixing it with water, a small quantity of this compound is precipitated. (Ullgren.)—2. By digesting trisulphate of mercuric oxide with sulphate of ammonia, till the undissolved portion turns white. In this reaction, soluble sulphate of mercuric oxide and ammonia is produced at the same time. (Ullgren.)

$$2(3HgO,SO^3) + 3(NH^3,SO^3) = (Hg,NH^2 + 3HgO,SO^3) + 2(NH^3,SO^3 + HgO,SO^3) + HO.$$

Heavy white powder (Kane); somewhat yellowish after drying. (Ullgren.) The compound turns brown when heated, gives off a large quantity of water and nitrogen, and a trace of ammonia, and leaves mercurous sulphate. [2 atoms of mercury must likewise be given off:

$$Hg,NH^2 + 3HgO,SO^3 = Hg^2O,SO^3 + 2Hg + 2HO + N].$$

Hydrosulphuric acid gas passed through water in which the powder is suspended, produces sulphide of mercury and a perfectly neutral solution of sulphate of ammonia. The sulphide of mercury amounts to 96·58 per cent., and the solution, when evaporated, yields 13·5 per cent. of sulphate of ammonia, containing 3·48 ammonia, 8·18 sulphuric acid, and 1·84 water. (Kane.) Water dissolves but a trace of the powder, but it is soluble in hydrochloric or nitric acid. (Kane, *Ann. Chim. Phys.* 72, 228.) When treated with hydrosulphate of potash, it gives off ammonia, but not when treated with caustic potash. With nitric acid it forms a solution containing ammonia, while nitrous fumes are given off. (Ullgren, *Pogg.* 42, 395.)

| | | | | | Kane. |
|---|---|---|---|---|---|
| $4Hg$ | 400 | .... | 83·34 | .... | 83·43 |
| $NH^2$ | 16 | .... | 3·33 | .... | 3·27 |
| $3O$ | 24 | .... | 5·00 | .... | |
| $SO^3$ | 40 | .... | 8·33 | .... | 8·25 |
| $Hg,NH^2 + 3HgO,SO^3$ | 480 | .... | 100·00 | | |

Instead of amide of mercury, a compound not known in the separate state, we may suppose that this and several of the following compounds contain nitride of mercury, a compound which can be obtained in the free state. On this hypothesis, the formula of the substance under consideration is: $Hg^3N + HgO,SO^3 + 2$ Aq. (Rammelsberg, *Pogg.* 15, 85.) [In the preceding compound M, supposing its composition to have been rightly determined, this transformation of the formula requires us to assume the existence of a nitride having the formula $Hg^6N$.]

O. Sulphate of Mercuric Oxide and Ammonia.—A neutral solution of mercuric sulphate, concentrated as much as possible, gives a white precipitate with sulphate of ammonia. (Fourcroy, *Ann. Chim.* 14, 34.) The solution of mercuric sulphate in oil of vitriol (not that of the nitrate or chloride in water) is likewise precipitated white by sulphate of ammonia. (Gm.) Mercuric oxide dissolves in cold aqueous sulphate of ammonia, and is not precipitated from the solution by ammonia. If mercurous oxide be used, the application of heat is necessary, and mercury separates out. (Wittstein, *Repert.* 57, 70.) ¶ Hirzel (*Zeitschr. f. Pharm.* 1850, 17) obtains this salt in large crystals, belonging to the oblique prismatic system, by dissolving 1 At. anhydrous mercuric sulphate in warm sulphuric acid, digesting the liquid with a solution of 1 At. sulphate of ammonia till the precipitate first formed re-dissolves, then adding boiling water till a permanent turbidity is produced, and leaving the whole to cool slowly. The crystals blacken when exposed to light. Hirzel is also of opinion that his crystals contained ammoniacal turpethum; but his analyses do not agree well with each other. ¶

P. Ammonio-diniodide of Mercury, or Iodo-mercurite of Ammonia.—Diniodide of mercury immersed in cold aqueous ammonia is converted into a black powder which gives off nearly all its ammonia in drying. On boiling with ammonia, a blackish powder is obtained mixed with a large number of globules of mercury, and a liquid from which iodide of mercury and ammonium separates. (Rammelsberg, *Pogg.* 48, 184.)

Q. Ammonio-protiodide of Mercury, or Iodo-mercurate of Ammonia.—*With* 1 *At. Acid.*—100 parts of mercuric iodide absorb 7·01 pts. of ammonia. The dirty white compound gives off ammonia in the air in a few hours, receiving at the same time the red colour of mercuric iodide. (H. Rose, *Pogg.* 20, 161).

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| $NH^3$ | 17 | .... | 7·00 | .... | 6·55 |
| HgI | 226 | .... | 93·00 | .... | 93·45 |
| $NH^3$,HgI | 243 | .... | 100·00 | .... | 100·00 |

*b. With* 2 *At. Acid.*—1. Mercuric iodide immersed in strong ammonia turns white, and then dissolves, leaving a red-brown powder (consisting of the following compound R): the solution evaporated in the air deposits needles of Q, *b*, while hydriodate of ammonia remains in solution. (Caillot & Corriol, *J. Pharm.* 9, 381; also *Schw.* 39, 379.)—2. The same compound is formed when the ammonia is allowed to act till the iodide of mercury is converted into a white powder. (Rammelsberg, *Pogg.* 48, 170.) 3. It is also produced when the solution of mercuric iodide in aqueous sulphide of ammonium, potassium, or sodium is precipitated by ammonia. (Rammelsberg.)

By (1), small needles (Caillot & Corriol); by (2) and (3), white crystalline powder. The compound quickly gives off its ammonia when exposed to the air, leaving protiodide of mercury,—still more quickly when immersed in water or in dilute acids. (Caillot & Corriol; Rammelsberg.)

| | *Crystallized.* | | | | Rammelsberg. |
|---|---|---|---|---|---|
| $NH^3$ | 17 | .... | 3·62 | .... | 3·614 |
| 2HgI | 452 | .... | 96·38 | .... | 95·540 |
| HO | | .... | | .... | 0·846 |
| $NH^3,2HgI$ | 469 | .... | 100·00 | .... | 100·000 |

R. Mercuric Amido-iodide, or Hydrated Mercuric Nitro-iodide. —$Hg,NH^2+HgI+2HgO$, or $Hg^3N,HgI+2Aq$.—1. Iodide of mercury heated with a very large excess of strong ammonia, assumes at first a lighter red colour, becoming indeed almost white; but afterwards, even at 60°, quickly turns brown, and on boiling becomes dark-coloured, like mineral kermes. The liquid filtered from it deposits needles of Q, *b*, and holds in solution hydriodate of ammonia, together with a small quantity of mercuric iodide:

$$4HgI+4NH^3+2HO=3(NH^3,HI)+(Hg,NH^2+HgI+2HgO).$$

To obtain the brown compound pure, the ammonia must be decanted at a boiling heat, before it deposits crystals, and the residue must be heated from five to seven times to the boiling point with fresh ammonia, till the decanted liquid deposits no more crystals on cooling; if this be not done, the brown compound will retain a portion of the white compound Q, *b*.—2. The compound is also formed by passing ammoniacal gas at a temperature of 180° over mercuric oxy-iodide:

$$HgI,3HgO+NH^3=(Hg,NH^2+HgI+2HgO)+HO.$$

3. Also when the yellow chlorine-compound, of exactly similar constitution, obtained in washing white precipitate, is digested with 1 At. aqueous iodide of potassium:

$$(Hg,NH^2+HgCl+2HgO)+KI=(Hg,NH^2+HgI+2HgO)+KCl.$$

Brown powder, often inclining to purple-red. When heated to 128°, it gives off nothing but a little hygroscopic water.

| | | | | | Rammelsberg. |
|---|---|---|---|---|---|
| 4Hg | 400 | .... | 71·69 | .... | 72·09 |
| N | 14 | .... | 2·51 | .... | 2·66 |
| 2H | 2 | .... | 0·36 | .... | |
| I | 126 | .... | 22·58 | .... | |
| 2O | 16 | .... | 2·86 | .... | |
| | 558 | | 100·00 | | |

When strongly heated in a retort, out of contact of air, it fuses into a dark brown liquid, afterwards detonates briskly with a blue light, and gives off mercury, iodide of mercury, ammonia, and nitrogen gas, leaving no residue. When heated with aqueous sulphide of barium, it gives off all its nitrogen in the form of ammonia, which amounts to 3·24 per cent. In warm aqueous iodide of potassium, it dissolves, with evolution of ammonia, forming a yellow-liquid, which contains free potash, besides iodide of mercury and potassium:

$$(Hg,NH^2+HgI+2HgO)+7KI+HO=4(KI,HgI)+NH^3+3KO.$$

When heated to 100° in a current of hydrochloric acid gas, it becomes dotted with yellow stars, and emits white fumes. If the heat rises to the fusing and subliming point, a sublimate is formed, consisting of chloromercurate of ammonia, protochloride of mercury, sal-ammoniac, and hydriodate of ammonia. Formation of water has not been distinctly observed. The compound dissolves with tolerable facility in warm hydrochloric acid, forming a colourless liquid, which, if concentrated, deposits on cooling, red crystals of mercuric iodide, and likewise yellow crystals of mercuric chloriodide. Boiling solution of potash exerts no decomposing action upon it, and therefore does not liberate ammonia from it. (Rammelsberg, *Pogg.* 48, 173.)

S. Iodide of Mercury and Ammonium.—The aqueous solution of 144 pts. (1 At.) of hydriodate of ammonia dissolves, with the aid of heat, 683 pts. (3 At. $3 \times 226 = 678$) of mercuric iodide. Part of the latter separates again on cooling, and the remaining liquid afterwards yields crystals of the bi-acid salt. These crystals are permanent in the air. In vacuo, they give off 3·8 per cent. of water, and acquire an orange-yellow colour. At a gentle heat, they fuse into a liquid which gives off, with ebullition, about 3 per cent. of water, becoming more tenacious, and acquiring a dark red colour, and on cooling, solidifies in anhydrous crystals, which, after a while, assume the red colour of mercuric iodide. At a stronger heat, part of the salt sublimes undecomposed; the rest is resolved into mercury, mercuric iodide, and other products. Water separates from the crystals 40 per cent. of mercuric iodide, so that the remaining solution no longer contains quite 1 At. iodide of mercury to 1 At. hydriodate of ammonia. This solution, when evaporated and cooled, again yields crystals of the bi-acid salt, so that an excess of hydriodate of ammonia remains in the liquid. (P. Boullay, *Ann. Chim. Phys.* 34, 345.)

| | *Anhydrous.* | | | | *Crystallized.* | | | |
|---|---|---|---|---|---|---|---|---|
| $NH^3,HI$ | 144 | .... | 24·16 | | $NH^3,HI$ | 144 | .... 23·45 | .... 24·3 |
| 2HgI | 452 | .... | 75·84 | | 2HgI | 452 | .... 73·62 | .... 71·9 |
| | | | | | 2HO | 18 | .... 2·93 | .... 3·8 |
| $NH^3,HI + 2HgI$ | 596 | .... | 100·00 | | + 2Aq. | 614 | .... 100·00 | .... 100·0 |

T. Ammonio-bromide of Mercury, or Bromo-Mercurate of Ammonia.—Cold protobromide of mercury does not absorb ammoniacal gas at ordinary temperatures; but when fused at a gentle heat in that gas, and then cooled, it absorbs 3·41 per cent., or less than $\frac{1}{2}$ At. ammonia. It is certain, however, that the quantity of ammonia found by experiment was too small, because some of the mercuric bromide must have evaporated. (H. Rose, *Pogg.* 20, 160.) Water extracts hydriodate of ammonia from the compound, and leaves a yellow powder, which gives off ammonia when treated with sulphide of potassium, but not with caustic potash. (Rammelsberg, *Pogg.* 55, 248.)

U. Amido-bromide of Mercury.—Ammonia added to an aqueous solution of mercuric bromide, throws down a white powder, insoluble in water and alcohol, slightly soluble in ammonia. When heated, it is resolved into nitrogen gas, ammoniacal gas, vapour of water, and a sublimate of mercurous bromide. (Löwig.) When very slowly heated, it gives off a large quantity of ammoniacal gas without free nitrogen,

afterwards a sublimate of $NH^3,2HgBr$, and leaves a residue of $Hg^3N,2HgBr$:

$$6(Hg,NH^2+HgBr)=3NH^3+NH^3,2HgBr+2(Hg^3N,2HgBr).$$

(Mitscherlich, *J. pr. Chem.* 19, 455.)

V. Bromide of Mercury and Ammonium.—Mercuric bromide dissolves abundantly in aqueous hydrobromate of ammonia; alkaline carbonates added to the solution, precipitate the compound U. (Löwig.)

W. *Bromate of Mercurous Oxide with Ammonia?*—Recently precipitated bromate of mercurous oxide yields, with excess of ammonia, a black substance and a liquid.—The black substance retains its colour when washed and dried in the air; it contains from 74·76 to 75·02 per cent. of mercurous oxide and a small quantity of metallic mercury. With potash, it gives off only part of its ammonia, with sulphide of potassium, the whole, amounting to between 1·86 and 2·22 per cent. It dissolves in hydrochloric acid with violent evolution of bromine and chlorine, and forms a yellow solution; hot nitric acid converts it into a white insoluble compound, which appears to be nitrate of mercuric oxide and ammonia. —The ammoniacal liquid, when left to stand, deposits mercury and bromate of mercuric oxide and ammonia; when evaporated at a gentle heat, it yields crystals of bromate of ammonia, while the mother-liquid contains mercury. (Rammelsberg.)

X. Mercuric Bromate with Mercuric Amide, or Hydrated Bromate of Mercuric Oxide with Nitride of Mercury.—$HgNH^2+3HgO,BrO^5$, or $Hg^3N+HgO,BrO^5+2Aq$.—When aqueous mercuric bromate is slightly supersaturated with ammonia, this compound is produced in the form of a precipitate, which slowly settles down. The filtrate contains bromate of ammonia.—The compound, when heated in a glass tube, detonates violently, even in small quantity, breaking the tube, and scattering metallic mercury about. When boiled with aqueous sulphide or iodide of potassium, it gives off 3·335 per cent. of ammonia, but with caustic potash only a trace. (Rammelsberg, *Pogg.* 55, 82.)

| | | | | | Rammelsberg. |
|---|---|---|---|---|---|
| 4Hg | 400·0 | .... | 71·63 | .... | 71·52 |
| N | 14·0 | .... | 2·51 | .... | 2·75 |
| 2H | 2·0 | .... | 0·36 | .... | |
| 3O | 24·0 | .... | 4·30 | .... | |
| $BrO^5$ | 118·4 | .... | 21·20 | .... | |
| | 558·4 | .... | 100·00 | | |

Y. Ammonio-dichloride of Mercury, or Chloro-mercurite of Ammonia.—Sublimed calomel absorbs a very small quantity of ammonia, and turns quite black. Calomel, prepared in the humid way, absorbs 7·38 per cent., and forms a black powder, which, on exposure to the air or when gently heated, gives off all its ammonia and turns white again; and on the application of a stronger heat, sublimes as pure calomel. (H. Rose, *Pogg.* 20, 158.)

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 6·74 | .... | 6·87 |
| $Hg^2Cl$ | 235·4 | .... | 93·26 | .... | 93·13 |
| $NH^3,Hg^2Cl$ | 252·4 | .... | 100·00 | .... | 100·00 |

Z. Mercurous Amido-chloride.—Calomel treated with aqueous ammonia, is converted into a powder, which is black while moist and dark grey when dry. Half the chlorine of the calomel is found in the ammoniacal liquid. (Kane.)

| | | | | | Kane. |
|---|---|---|---|---|---|
| 4Hg | 400 0 | .... | 88·61 | .... | 88·33 |
| $NH^2$ | 16·0 | .... | 3·55 | .... | 3·36 |
| Cl | 35·4 | .... | 7·84 | .... | 7·95 |
| $Hg^2,NH^2 + Hg^2Cl$.. | 451·4 | .... | 100·00 | .... | 99·64 |

Heated in a glass tube, it first gives off a trace of water, together with a large quantity of nitrogen and ammoniacal gas, and afterwards a sublimate of calomel and mercury, exhibiting at the same time a glimmering light. Probably thus:

$$3(Hg^2,NH^2 + Hg^2Cl) = 6Hg + 3Hg^2Cl + 2NH^3 + N.$$

It undergoes no alteration when heated in the air to 82°, or by continued boiling with water or ammonia.—When boiled with aqueous iodide of potassium, it gives off all its nitrogen in the form of ammonia; with caustic potash, it evolves only a part. (Kane, *Phil. Mag. J.* 11, 504; also *Pogg.* 42, 330; also *Ann. Pharm.* 18, 298.)—When hydrochloric acid gas is passed over the powder previously dried in the air at 100°, it is converted, without forming even a trace of aqueous hydrochloric acid (which proves the absence of oxygen) into a white mixture of mercurous chloride and sal-ammoniac (Ullgren, *Pogg.* 42, 392):

$$Hg^2NH^2 + Hg^2Cl + 2HCl = 2Hg^2Cl + NH^3,HCl.$$

According to this, 451·4 pts. (1 At.) of the compound should yield 524·2 pts. of the white mixture; Ullgren obtained 523·8 pts., a quantity which is perfectly in accordance with Kane's formula, and proves that the compound contains not ammonia, but amidogen.

AA. Ammonio-protochloride of Mercury, or Chloro-mercurate of Ammonia.—1. Formed by exposing heated corrosive sublimate to a current of ammoniacal gas. At ordinary temperatures, the compound is very slowly absorbed, the quantity amounting to only 5·75 per cent. in two days; but if fused at a gentle heat and then cooled, the sublimate immediately takes up 6·8 per cent. (H. Rose.) Grouvelle had previously found that 2 atoms of corrosive sublimate take up 1 atom of ammonia.—2. By distilling mercuric oxide with sal-ammoniac. (Mitscherlich.)

The compound resembles corrosive sublimate, fuses when heated, sublimes in drops like that substance, and without much loss of ammonia. It does not dissolve in water, but turns yellowish when boiled with that liquid for a considerable time; solution of potash likewise colours it pale-yellow. (H. Rose, *Pogg.* 20, 158.)—With water it is resolved into alembroth-salt, which dissolves, and infusible white precipitate, which remains undissolved. (Kane.)

$$2(NH^3,2HgCl) = (Hg,NH^2 + HgCl) + (2HgCl + NH^4Cl).$$

According to Grouvelle (*Schw.* 33, 433), it dissolves partially in water, with separation of mercurate of ammonia [?], a further quantity of which may be precipitated from the solution by potash.

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 5·91 | .... | 6·37 |
| 2HgCl | 270·8 | .... | 94·09 | .... | 93·63 |
| $NH^3,2HgCl$ | 287·8 | .... | 100·00 | .... | 100·00 |

May likewise be regarded as $HgAd,HCl+HgCl$ (Kane),—or, taken twice, as $HgNH^2+3HgCl+NH^4Cl$,—or, taken three times, as $Hg^3N, HCl+3HgCl+2(NH^4Cl)$.

BB. Mercuric Amido-chloride.—Formerly regarded, according to Hennel's formula, as a compound of 2 At. mercuric oxide with 1 At. sal-ammoniac, till Kane showed that 2 At. oxygen and 2 At. hydrogen must be deducted therefrom.—It was, moreover, confounded with the following compound, under the name of *White Precipitate*, *Mercurius præcipitatus albus*, till Wöhler (*Ann. Pharm.* 26, 203) and Kane pointed out the difference between the two varieties. The compound immediately under consideration may be distinguished by the name of *Infusible White Precipitate*. The white precipitate of the Baden pharmacopœia belongs to this head.

Infusible white precipitate is formed, by precipitating corrosive sublimate with a slight excess of ammonia, washing the precipitate with a small quantity of cold water, pressing between paper, and drying at a gentle heat. (Kane):

$$2HgCl+2NH^3=HgCl,HgNH^2+NH^4Cl.$$

272 pts. (2 At.) dissolved corrosive sublimate, precipitated by aqueous ammonia, containing 34 pts. (2 At.) of ammonia, yield a neutral filtrate, which leaves 1 At. sal-ammoniac on evaporation. (Hennel, *Qu. J. of Sc.* 18, 297.) 270·8 pts. (2 At.) corrosive sublimate yield 252·2 pts. (1 At. = 251·4) of white precipitate, and the filtrate contains 35·2 pts. (1 At.) of chlorine. (Kane.) 270·8 pts. of corrosive sublimate yield 254·6 pts. of white precipitate dried at a gentle heat. (Geiseler, *N. Br. Arch.* 21, 147.) The flocculent precipitate must not be washed too long, more particularly with hot water, as it then turns yellowish from admixture of the compound DD (p. 88.) (Kane.) White precipitate is likewise obtained on precipitating corrosive sublimate with carbonate of ammonia. (Duflos.) According to Winckler, it is also formed by agitating mercuric oxychloride with strong ammonia. [Might not mercurate of ammonia be mixed with the product thus obtained?]

White and tolerably light powder, the taste of which is earthy at first, but afterwards metallic. (Fourcroy.)

| | | | Kane. | | Riegel. | | Hennel. | Fourcroy. |
|---|---|---|---|---|---|---|---|---|
| 2Hg | 200·0 | 79·56 | 78·60 | | 78·85 | | 74·08 | 75 |
| N | 14·0 | 5·57 | 6·37 | | 6·35 | | 5·24 | |
| 2H | 2·0 | 0·79 | | | | | | |
| Cl | 35·4 | 14·08 | 13·85 | | 13·86 | | | |
| HO | | | 0·58 | | | | | |
| | 251·4 | 100·00 | 99·40 | | 99·06 | | | |

Soubeiran (*J. Pharm.* 12, 243; also *N. Tr.* 13, 2, 161), obtained 82 per cent. mercury and only 7·9 per cent. chlorine, probably from washing too long, whereby a considerable quantity of the yellow compound DD would be formed:

$Hg,NH^2+HgCl$ (Kane), or $Hg^3N+HgCl+NH^4Cl$ (Rammelsberg).

¶ The simplest view of its composition is to regard it as chloride of ammonium in which 2 atoms of hydrogen are replaced by mercury: $N\left(\begin{matrix}H_2\\Hg_2\end{matrix}\right)Cl$. ¶

*Decompositions.* At a temperature below redness, it is resolved, without fusion (but with production of a yellowish colour), into a sublimate of calomel, amounting to 93 per cent., and a mixture of 1 volume of nitrogen and 2 volumes of ammoniacal gas (Kane):

$$3(HgNH^2 + HgCl) = 3Hg^2Cl + N + 2NH^3.$$

The calomel is usually blackened by the ammonia. If the heat applied is very gentle, ammonia is first evolved, without a trace of nitrogen; afterwards chloromercurate of ammonia sublimes (distinguishable from the calomel by its fusibility before evaporation), and chloronitride of mercury EE (p. 89) remains in the retort in the form of a red substance:

$$6(HgNH^2 + HgCl) = 3NH^3 + NH^3,2HgCl + 2(Hg^3N,2HgCl).$$

(E. Mitscherlich, *J. pr. Chem.* 19, 454.) Heated with aqueous sulphide of barium, or iodide of potassium, it gives off all its nitrogen in the form of ammonia, and leaves sulphide or iodide of mercury. (Kane.) A boiling saturated solution of chloride of potassium or sodium, likewise separates ammonia from the compound, and dissolves corrosive sublimate. (Rammelsberg, *Pogg.* 48, 182.) With potash or lime, it turns yellowish, gives off only half the quantity of ammonia that it is capable of yielding, and produces the yellow powder DD, but of a somewhat paler colour than that obtained by other methods. (Kane.) Ammonia has no action upon it. (Kane.) Does not dissolve in water, but turns yellowish when immersed in it. By boiling water it is completely converted, in a few minutes, into the lemon-yellow powder DD, while sal-ammoniac dissolves in the water:

$$2(Hg,NH^2 + HgCl) + 2HO = (HgNH^2 + HgCl + 2HgO) + NH^4Cl.$$

502·8 pts. (2 At.) of white precipitate yield by boiling with water 450·5 pts. (nearly 1 At.) of the yellow powder, and the water is found to have dissolved 51·5 pts. (nearly 1 At.) of sal-ammoniac. (Kane, *Phil. Mag. J.* 8, 495; 11, 428; also *Pogg.* 42, 367: also *Ann. Pharm.* 18, 135 and 288; also *J. pr. Chem.* 8, 219.) When dry hydrochloric acid gas is passed over the compound previously dried at 100°, in the air, or at the ordinary temperature in vacuo, and the temperature is raised first to 100°, then somewhat higher, the whole is converted, without evolution of water, into a fused transparent mixture of mercuric chloride and sal-ammoniac:

$$(HgNH^2 + HgCl) + 2HCl = 2HgCl + NH^4Cl.$$

In this reaction, nothing sublimes but a small quantity of corrosive sublimate and sal-ammoniac, not a trace of aqueous hydrochloric acid. 251·4 pts. (1 At.) of white precipitate yield from 320·6 to 323·5 of this fused mixture; according to calculation, the quantity should be $2 \cdot 135{\cdot}4 + 53{\cdot}4 = 324{\cdot}2$. This result confirms Kane's analysis. (Ullgren, *Pogg.* 42, 385; also *Ann. Pharm.* 26, 203.) The compound boiled with excess of aqueous protochloride of copper, yields Brunswick green (V., 441), and a solution of alembroth-salt:

$$3(HgNH^2 + HgCl) + 8CuCl + 6HO = 2(CuCl,3CuO) + 3(2HgCl,NH^4Cl).$$

(Kane, *Ann. Chim. Phys.* 72, 382.) White precipitate dissolves easily in hydrochloric acid, forming a solution of mercuric chloride and sal-ammoniac, and in sulphuric or nitric acid, forming mercuric chloride and sulphate or nitrate of mercuric oxide and ammonia. (Fourcroy.) It is easily soluble in aqueous hydrocyanic acid. (Hennel.) Also in warm aqueous hydrochlorate or nitrate of ammonia. (Brett.)

CC. Mercuric Amido-chloride with Sal-ammoniac. — *Fusible White Precipitate.*—The white precipitate, or *Mercurius præcipitatus albus*, of the Prussian, Hanoverian, London, and several other pharmacopœias.—1. Formed by dropping a solution of corrosive sublimate into a boiling aqueous mixture of sal-ammoniac and ammonia, as long as the precipitate redissolves, and leaving the solution to cool to the crystallizing point. The product is sometimes contaminated with a small quantity of the infusible white precipitate BB. (E. Mitscherlich, *J. pr. Chem.* 19, 453.)—2. The same compound is precipitated on adding carbonate of potash or soda, not in too great excess, to a cold aqueous solution of equal parts of corrosive sublimate and sal-ammoniac. This is the mode of preparation recommended in the pharmacopœias. 135·4 pts. (1 At.) of corrosive sublimate dissolved in water, together with an equal quantity of sal-ammoniac, required for complete precipitation 260 pts. (nearly 2 At. = 286·4) of crystallized carbonate of soda, and yield 140·8 pts. of well dried white precipitate, the liquid retaining 2·03 parts of mercury in solution. (Geiseler.) [According to Kane's analysis, 135·4 pts. of corrosive sublimate should yield 152·4 pts. of white precipitate, if no mercury remained in solution.] If 960 instead of 260 parts of crystallized carbonate of soda be used for the precipitation, the precipitate is of a less pure white, and, when washed on the filter, becomes yellow on the surface, but recovers its whiteness when washed with water containing sal-ammoniac. The yellow colour is more quickly produced when the carbonate of soda is added in excess and the liquid is hot. (Geiseler, *N. Br. Arch.* 21, 147.) The same substance is obtained by precipitating the solution of sal-ammoniac and corrosive sublimate with carbonate of ammonia. (Duflos.)—3. This compound is likewise formed on boiling the infusible white precipitate BB with sal-ammoniac. (Kane.) Red mercuric oxide has no action on a cold solution of sal-ammoniac; in a hot solution, it acquires a pale yellow colour, if 29·5 pts. of sal-ammoniac are present for every 108 pts. of oxide; if 59 pts. of sal-ammoniac are present for every 108 of the oxide, the latter is converted into white precipitate. (Geiger, *Mag. Pharm.* 11, 153.) When the sal-ammoniac is in excess, fusible white precipitate is produced. (Gm.)

When prepared by (1) it forms small rhombohedrons (Mitscherlich); (2), a white powder.

When heated, it fuses (forming a clear, yellowish liquid, according to Wöhler), giving off nitrogen and ammonia, and then sublimes, partly in the form of a transparent, gummy mass, partly as a white, opaque mass, which, when treated with water, yields a solution of sal-ammoniac and corrosive sublimate, and a residue of calomel. If the precipitate has been previously well dried, it does not yield a trace of water when thus treated. (Kane, *Ann. Chim. Phys.* 72, 380.) The precipitate undergoes no alteration at 135°; at 180°, it yields ammonia and a white sublimate, and at 300°, fuses into a thin, yellowish liquid. (Duflos, *N. Br. Arch.* 23, 311.) If the application of heat be stopped as soon as the evolution of ammonia ceases, the liquid, which has already acquired a dark colour, solidifies in a red-brown, fibrous mass. (Krug & Vahle, *N. Br. Arch.* 27, 40.) Boiling water converts fusible white precipitate into the yellow powder DD, the same that is formed by similar means from infusible white precipitate; in the former case, however, the water takes up a much larger quantity of sal-ammoniac. (Kane.) The precipitate is dissolved by acids, even by strong acetic acid.

| | A. | | | | Kane. |
|---|---|---|---|---|---|
| 2Hg | 200·0 | .... | 65·62 | .... | 65·81 |
| 2N | 28·0 | .... | 9·19 | .... | 8·96 |
| 6H | 6·0 | .... | 1·96 | .... | 1·92 |
| 2Cl | 70·8 | .... | 23·23 | .... | 22·57 |
| | 304·8 | .... | 100·00 | .... | 99·26 |

| | B. | | | | Duflos. | | Riegel. |
|---|---|---|---|---|---|---|---|
| 3Hg | 300·0 | .... | 70·89 | .... | 69·47 | .... | 69·23 |
| N | 14·0 | .... | 3·31 | .... | 3·24 | .... | 3·16 |
| 3H | 3·0 | .... | 0·71 | .... | 0·69 | .... | 0·68 |
| 3Cl | 106·2 | .... | 25·09 | .... | 24·30 | .... | 24·23 |
| | 423·2 | .... | 100 00 | .... | 97·70 | .... | 97·30 |

Calculation A, founded on Kane's analysis, gives either the formula: $NH^3,HgCl$, or $Hg,NH^2+HgCl+NH^4Cl$, or $Hg^3N+HgCl+3(NH^4Cl)$. From the resemblance between the reactions of this compound and that of the infusible white precipitate, it is probable that one of the last two formulæ is the true expression of its composition.—¶ The simpler formula, $N\left(\begin{matrix}H_3\\Hg\end{matrix}\right)Cl$, which denotes that the compound may be regarded as sal-ammoniac, in which 1 atom of hydrogen is replaced by mercury, brings into still stronger light the analogy between this compound and the infusible white precipitate BB, which, as already observed (p. 85), may be expressed by the formula $N\left(\begin{matrix}H_2\\Hg_2\end{matrix}\right)Cl$. ¶—There must either be a third kind of white precipitate corresponding to the analyses of Duflos and Riegel, or there must be some mistake in these analyses.

DD. Mercuric Amid-oxychloride.—$Hg,NH^2 + HgCl + 2HgO$.—Formed by boiling either the infusible or the fusible white precipitate with water. 541·6 pts. (4 At.) corrosive sublimate, precipitated by ammonia, and boiled till the precipitate is completely converted into the light yellow powder, yield 454 pts. (nearly 1 At.) of yellow powder; the liquid contains 102·3 pts. (nearly 3 At.) of chlorine, together with a trace of mercury. Another mode of preparation consists in boiling white precipitate with caustic potash. (Kane.)—The same compound is likewise produced when dry ammoniacal gas is passed at a temperature of 150° over, $HgCl,3HgO$ previously dried at 100°. (Ullgren.)

Light yellow, heavy powder, granular after rapid drying. That which is obtained by boiling with potash is of a paler yellow colour, and detonates somewhat more strongly when suddenly heated. (Kane.)

| | | | | | Kane. |
|---|---|---|---|---|---|
| 4Hg | 400·0 | .... | 85·58 | .... | 86·23 |
| N | 14·0 | .... | 2·99 | } | 3·60 |
| 2H | 2·0 | .... | 0·43 | } | |
| Cl | 35·4 | .... | 7·58 | .... | 7·77 |
| 2O | 16·0 | .... | 3·42 | .... | |
| | 467·4 | .... | 100·00 | | |

$Hg,NH^2+HgCl+2HgO$.—May likewise be regarded as $Hg^3N+HgCl+2HO$ (Rammelsberg),—or as $NHg^4Cl+2HO$, analogous to chloride of ammonium [W].

When gradually heated, it gives off ammonia, nitrogen gas, and water, and subsequently a sublimed mixture of calomel and mercury, amounting to 94·01 per cent. No mercuric oxide remains behind.

(Kane.)—With aqueous sulphide of potassium, it evolves ammoniacal gas, and forms sulphide of mercury.—Heated with aqueous iodide of potassium, it turns brown and gives off ammonia. (Kane.) The brown substance formed in this reaction, is the iodine-compound corresponding to the yellow powder (p. 81), and the evolution of ammonia is merely a secondary effect produced by the action of the excess of iodide of potassium upon the brown compound. A saturated solution of chloride of potassium or sodium, boiled with the yellow powder, also liberates ammonia and takes up mercury. (Rammelsberg, *Pogg.* 48, 181.)—Concentrated nitric acid which has been completely freed by heat from hyponitric acid, and therefore gives off no nitrous fumes when heated with nitrate of ammonia or with corrosive sublimate, produces these fumes again on being heated with the yellow powder. (Ullgren, *Pogg.* 42, 385.)—Boiling potash-ley gives off no ammonia, exerts no decomposing action, and produces but a slight alteration of colour. (Kane, Ullgren.)—The yellow powder dissolves but slightly in water, but easily in hydrochloric or nitric acid. (Kane, *Pogg.* 42, 367.)

EE. Nitrochloride of Mercury.—Remains behind when infusible white precipitate is very carefully heated in a retort immersed in a bath of fusible metal, till all the ammonia is driven off, and the whole of the chloro-mercurate of ammonia is sublimed, and a small quantity of calomel begins to sublime. (*Comp.* pp. 84, 85.)

Small, red, crystalline scales, resembling mercuric oxide.

When heated to a temperature above the boiling point of mercury, it is resolved into nitrogen gas and a sublimate of calomel and mercury:

$$Hg^3N,2HgCl = N + Hg + 2Hg^2Cl.$$

Dissolves in boiling hydrochloric acid without evolution of gas, forming sal-ammoniac and corrosive sublimate:

$$Hg^3N,2HgCl + 4HCl = 5HgCl + NH^4Cl.$$

Boiling oil of vitriol exerts a similar action.—The compound is not dissolved or decomposed by boiling even with strong nitric acid, or with dilute sulphuric acid, or with alkalis, or with water. (E. Mitscherlich, *J. pr. Chem.* 19, 453.)

| *Calculation*, according to Mitscherlich. | | | |
|---|---|---|---|
| 5Hg | 500·0 | .... | 85·50 |
| N | 14·0 | .... | 2·39 |
| 2Cl | 70·8 | .... | 12·11 |
| $Hg^3N,2HgCl$ | 584·8 | .... | 100·00 |

FF. Protochloride of Mercury and Ammonium.—*a.* With excess of sal-ammoniac.—*Salt of Wisdom*, *Sal Alembroth* of the alchemists.—Usually prepared by dissolving equal parts of corrosive sublimate and sal-ammoniac in water, and evaporating the solution. This proportion gives nearly 3 At. sal-ammoniac to 1 At. corrosive sublimate.—A solution of corrosive sublimate and sal-ammoniac is likewise formed, with evolution of ammonia, on boiling a solution of sal-ammoniac with mercuric or mercurous oxide, metallic mercury being separated in the latter case; also on boiling the sal-ammoniac solution with mercuric or mercurous carbonate, the action being then attended with evolution of carbonate of ammonia. (Wittstein, *Repert.* 57, 70.)

135·4 pts. (1 At.) corrosive sublimate dissolve, at 15·6°, in 136 pts. of saturated solution of sal-ammoniac. [This solution, according to Karsten (II. 47), contains about 37 pts. of sal-ammoniac, so that the proportion

just mentioned gives about 3 At. corrosive sublimate to 2 At. sal-ammoniac.] The sal-ammoniac solution thus saturated with corrosive sublimate, still dissolves somewhat more than 37 parts of sal-ammoniac [thereby giving the proportion of 3 At. corrosive sublimate to 4 At. sal-ammoniac]. (J. Davy, *Phil. Trans.* 1822, 362.)

The solution of equal parts corrosive sublimate and sal-ammoniac in water, yields white precipitate when treated with caustic or carbonated alkalis. Spring water containing carbonate of lime, produces the same precipitate, slowly in the cold, immediately on the application of heat. Sugar throws down calomel from the solution, not in the cold, but at 87°. (Schindler, *Mag. Pharm.* 29, 265; *Repert.* 36, 238; *comp.* Winckler, *Repert.* 33, 196; 38, 255.)

*b. Mono-acid.*—$NH^4Cl, HgCl$.—1. The solution of equal parts of corrosive sublimate and sal-ammoniac yields, on evaporation and cooling, first, crystals of sal-ammoniac; afterwards, when the mother-liquid is further evaporated and cooled, an additional quantity of sal-ammoniac, together with crystals of the double chloride, which must be separated mechanically and purified by recrystallization. (Soubeiran.)—2. This compound is also formed when 1 At. (53·4 pts.) sal-ammoniac and 1 At. (135·4 pts.) corrosive sublimate are dissolved in a small quantity of boiling water—the solution left to cool—the mother liquid poured off from the crystals, which contain excess of corrosive sublimate—and evaporated in the hot-air chamber to the crystallizing point; the remaining mother-liquid, when evaporated either in the air or in vacuo, yields remarkably fine crystals. (Soubeiran, *J. Pharm.* 12, 184 and 231; also *N. Tr.* 13, 1, 201.)

Transparent, colourless, elongated rhombic prisms, sometimes with the terminal edges, sometimes with the obtuse summits perpendicularly truncated. They are permanent in the air, but become opaque at 40°, and gives off 5·5 per cent. of water at 100°.—When heated to partial sublimation, they are resolved into a sublimate richer in ammonia, and a residue richer in mercury.

The salt dissolves in 0·66 pt. water at 10°, and in nearly all proportions of boiling water. The boiling solution gives off a vapour having a metallic taste. With a small quantity of sulphuretted hydrogen, it yields a white, with a larger quantity, a black precipitate. With potash or soda, it gives off ammonia and yields a precipitate, but is not thrown down by ammonia. [It gives a white precipitate with ammonia: Gm.] It is not affected by sulphuric, hydrochloric, or nitric acid. (Soubeiran.)—A solution of 135·4 pts. (1 At.) corrosive sublimate, and 53·7 pts. (1 At.) sal-ammoniac, in 48 pts. ($5\frac{1}{3}$ At.) water, is liquid at about 41°, and when slowly cooled, deposits flattened four-sided prisms; if the quantity of water amounts to 144 pts. (16 At.), the solution has a specific gravity of 1·58, and remains liquid at 13°. (J. Davy.)

| | *Anhydrous.* | | | | *Crystallized.* | | | Soubeiran. |
|---|---|---|---|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 9·00 | $NH^3$ | 17·0 | .... | 8·60 | .... 9·0 |
| H | 1·0 | .... | 0·53 | H | 1·0 | .... | 0·50 | .... |
| Hg | 100·0 | .... | 52·97 | Hg | 100·0 | .... | 50·56 | .... 51·2 |
| 2Cl | 70·8 | .... | 37·50 | 2Cl | 70·8 | .... | 35·79 | .... 36·2 |
| | | | | HO | 9·0 | .... | 4·55 | .... 5·5 |
| | 188·8 | .... | 100·00 | | 197·8 | .... | 100·00 | |

*c. Bi-acid.*—1. Formed by subliming a mixture of 53·4 parts of sal-ammoniac and 270·8 parts of corrosive sublimate. (J. Davy.)—2. By

dissolving the same mixture in water, and leaving the solution to crystallize. The crystals obtained are sometimes anhydrous, sometimes hydrated. (Kane.) The anhydrous salt separates in rhombohedrons. (Kane.) It is easily fusible, and, on cooling, solidifies in a greyish white mass, having a faint pearly lustre. The temperature at which it volatilizes is much higher than the subliming point of corrosive sublimate or sal-ammoniac alone; and its sublimation is attended with partial decomposition, so that the sublimed mass contains traces of calomel and hydrochloric acid. (J. Davy.)

The hydrated crystals are long silky needles. (Kane.) They have the same form as the corresponding potassium-salt (p. 101). (Mitscherlich, *J. pr. Chem.* 19, 453.) A solution of 1 At. of the anhydrous compound in 8 At. water is liquid at 60°, and solidifies in needles on cooling; a solution containing 16 At. water, forms at 29° a liquid of specific gravity 1·98, and solidifies at 13°. (J. Davy, *Phil. Trans.* 1822, 362.)

| *Anhydrous.* | | | | *Hydrated.* | | | |
|---|---|---|---|---|---|---|---|
| $NH^4Cl$ | 53·4 | .... | 16·47 | $NH^3$ | 53·4 | .... | 16·02 |
| 2HgCl | 270·8 | .... | 83·53 | 2HgCl | 270·8 | .... | 81·28 |
| | | | | HO | 9·0 | .... | 2·70 |
| $NH^4Cl$,2HgCl | 324·2 | .... | 100·00 | + Aq. | 333·2 | .... | 100·00 |

GG. Basic Hydrofluate of Mercuric Oxide and Ammonia.—When aqueous ammonia is poured upon protofluoride of mercury, a white basic double salt is formed. (Berzelius.)

HH. Nitrate of Mercurous Oxide and Ammonia.—*a. Basic.—Hahnemann's Soluble Quicksilver, Mercurius Solubilis Hahnemanni.*—To form this compound, a very dilute solution of mercurous nitrate, which must be as free as possible from excess of nitric acid, and from mercuric nitrate, is precipitated in the cold by very dilute aqueous or alcoholic ammonia, added gradually and in less than equivalent quantity, the liquid being well stirred all the time; the precipitate is then quickly thrown upon a filter, washed with cold water, pressed between paper, and dried in the shade at ordinary temperatures. Even the first small quantities of ammonia do not throw down pure mercurous oxide, but a compound containing as much nitrate of ammonia as the portions subsequently precipitated. (C. G. Mitscherlich.) According to Soubeiran, the first precipitate contains nothing but mercurous oxide, with a small quantity of nitric acid, but no ammonia. According to Pagenstecher, the very first precipitate produced by an exceedingly small quantity of ammonia is lighter than that which is afterwards formed on the addition of more ammonia; Mitscherlich never observed this difference; a very small quantity of ammonia colours the solution dark brown. When the mercurous solution is supersaturated with ammonia, the filtrate contains basic nitrate of mercuric oxide and ammonia,* which separates out in crystals as the ammonia evaporates. (Pagenstecher.)

If the mercurous solution likewise contains mercuric oxide, basic nitrate of mercuric oxide and ammonia is precipitated at the same time, and causes the precipitate to exhibit a paler grey colour. If excess of nitric acid is present, a larger quantity of nitrate of ammonia is formed, which, when it acts in excess, decomposes part of the mercurous oxide in the pre-

* The compound designated in this and several other places by the old name of *basic nitrate of mercuric oxide and ammonia*, is probably $HgNH^2 + 2HgO,NO^5$.

cipitate into mercuric oxide and metallic mercury, in consequence of its greater affinity for mercuric than for mercurous oxide; so that the precipitate becomes mixed with mercury and basic nitrate of mercuric oxide and ammonia. For the same reason, it is necessary to filter immediately after precipitation. (C. G. Mitscherlich.)

If the ammonia acts in excess on particular parts of the solution, it decomposes the precipitate there produced—with greater facility in proportion as it is more concentrated—into metallic mercury and basic nitrate of mercuric oxide and ammonia, which dissolves in the excess of ammonia, but is afterwards precipitated as it mixes with the rest of the liquid. (C. G. Mitscherlich.) It is therefore necessary to use very dilute ammonia, pour it in by a tube drawn out to a fine point, and stir the liquid constantly. Pagenstecher and Pleischl likewise consider it disadvantageous to pour the ammonia on the surface of the liquid [probably because, being specifically lighter, it then mixes less easily with the other portion]; they therefore recommend pouring it in through a long-necked funnel, the beak of which may likewise be used as a stirrer.

If the quantity of ammonia added be such as nearly to saturate the nitric acid, the precipitate, which is at first nearly black, gradually acquires a lighter grey colour, partly because the mercurous solution is frequently mixed with mercuric oxide, and consequently a basic nitrate of mercuric oxide and ammonia is deposited as the acid becomes further saturated, partly because the same salt is produced by the action of excess of ammonia in particular parts of the liquid, and being at first dissolved by the more acid liquid, is afterwards precipitated on the addition of a larger quantity of ammonia. According to C. G. Mitscherlich, the decomposition into mercuric oxide and metallic mercury takes place long before the liquid acquires an alkaline reaction; hence it is necessary to leave a considerable quantity of the mercurous solution undecomposed. To avoid exceeding the proper quantity of ammonia, a decanted or filtered sample must be treated with fresh ammonia, to ascertain whether it still gives a black precipitate; or the quantity of ammonia must be determined before-hand, according to the quantity of mercurous nitrate, as recommended by Pagenstecher, Pleischl, and others.

To obtain a solution of mercurous nitrate as free as possible from mercuric oxide and excess of acid, the crystals of the sesquibasic or monobasic nitrate of mercurous oxide (pp. 71, 72) obtained by leaving cold nitric acid in contact with excess of mercury, and rinsed with cold water, must be agitated with a large quantity of lukewarm water, and the solution separated by decantation from the residual yellow bibasic salt. The latter may also be dissolved in lukewarm water, to which nitric acid is very cautiously added, just as the crystals of the sesquibasic or monobasic salt may likewise be immediately and completely dissolved in water to which acid is added; there is, however, great risk of adding too much acid, unless it be introduced in small portions, and the liquid well shaken after each addition, to insure that the quantity of acid is not yet sufficient for the complete solution of the basic salt. In the preparation of mercurous nitrate, according to Bucholz's method (pp. 73, 4), the admixture of mercuric oxide cannot be avoided with an equal degree of certainty. The presence of mercuric oxide in the mercurous solution is recognized by precipitating with common salt in the cold and filtering; any mercuric oxide that may be present passes into the filtrate in the form of mercuric chloride. (C. G. Mitscherlich.)

Special directions for the preparation of this compound may be found

in the pharmacopœias, and are likewise given by Bucholz (*Berl. Jahrb.* 1806, 207), Beissenhirtz and Brandes (*Br. Arch.* 1, 2, 294), Pagenstecher (*Repert.* 16, 406), Stein & Buchner (*Repert.* 16, 406), Monheim (*Repert.* 34, 191), Stoltze (*Berl. Jahrb.* 25, 1, 49), Pleischl (*Zeitschr. Phys. v. Wiss.* 3, 318), C. G. Mitscherlich (*Pogg.* 9, 399), Duflos (*N. Br. Arch.* 23, 309), and others. The method of Duflos is peculiar in this respect, that 1 part of highly rectified spirit of wine saturated with ammoniacal gas, and mixed with 12 parts of spirit of wine, is used for the precipitation, the mercurial solution being added to this liquid—stirring all the while—till the mixture slightly reddens litmus. This process yields a blacker preparation than the rest; for, according to Duflos, the tendency of the nitrate of ammonia produced in the reaction to decompose the precipitated mercurous oxide into metallic mercury and mercuric oxide, is less powerful in the alcoholic than in the aqueous solution. [After long standing, however, the precipitate assumes a lighter grey colour, even in the alcoholic solution.]

The compound is black or greyish-black while moist, and blackish-grey when dry. In the pure state, it does not yield any globules of mercury when pressed.

| | | | C. G. Mitscherlich. | Duflos. | Kane. |
|---|---|---|---|---|---|
| $3Hg^2O$ | 624 | 88·63 | 88·95 | 88·8 to 89·5 | 85·6 |
| $NH^3$ | 17 | 2·42 | 2·46 | | |
| $NO^5$ | 54 | 7·67 | 7·32 | | |
| HO | 9 | 1·28 | | | |
| $3Hg^2O + NH^4O,NO^5$ | 704 | 100·00 | | | |

If the quantity of ammonia required to neutralize the nitric acid contained in the solution be divided into 4 parts, and the liquid filtered after the addition of each portion, four different precipitates are obtained, as follows: the first is black, and after drying at 38°, contains 82·3 per cent. of mercury; the second is black, and contains 84·5 per cent. mercury; the third is dark grey, and contains 86·7 per cent. mercury; and the fourth has a lighter grey colour, and contains 89 per cent. mercury. The quantity of mercury contained in the first precipitate agrees with the formula $2Hg^2O + NH^3,NO^5$. (Kane, *Ann. Chim. Phys.* 72, 257 )

According to Soubeiran, Hahnemann's quicksilver is a variable mixture of basic mercurous nitrate and the salt to which he gives the name of *Protonitrate ammoniaco-mercuriel* (p. 96).

Hahnemann's quicksilver, when exposed to light, is gradually resolved into metallic mercury and basic nitrate of mercuric oxide. Heated in a glass tube, it sublimes without residue, and yields a sublimate consisting wholly of mercury. (Duflos.) According to Buchner, it yields an orange-yellow sublimate of basic mercuric nitrate. With caustic potash, it gives off a small quantity of ammonia (none, according to Soubeiran). Baryta-water deprives it of only part of its acid, but aqueous sulphide of barium takes away the whole, and drives out all the ammonia. (C. G. Mitscherlich.) With oil of vitriol, it gives off nitrous fumes. (Soubeiran.) Boiling hydrochloric acid dissolves it completely, forming a solution of protochloride of mercury and ammonium. (C. G. Mitscherlich.) Probably thus:

$$3Hg^2O + NH^3,NO^5 + 7HCl = 6HgCl + NH^4Cl + NO^2 + 6HO.$$

Cold dilute hydrochloric acid converts the preparation into calomel, and dissolves out mercuric oxide, which is almost always present in the form

of basic nitrate of mercuric oxide and ammonia, produced either during the preparation or afterwards. Cold hydrochloric acid sometimes gives rise to the formation of a detonating compound. (C. G. Mitscherlich.) Cold dilute nitric acid dissolves out mercurous oxide (Bucholz), or basic mercurous nitrate (Soubeiran), [or pure Hahnemann's quicksilver], and leaves a less soluble white salt [the basic nitrate of mercuric oxide and ammonia, which is generally mixed with the salt; Soubeiran, however, regards it as basic nitrate of mercurous oxide and ammonia]. Boiling acetic acid dissolves the whole, with the exception of a few globules of mercury. (Bucholz.) With aqueous ammonia, Hahnemann's quicksilver is resolved into metallic mercury, and soluble basic nitrate of mercuric oxide and ammonia. (C. G. Mitscherlich.) It behaves in a similar manner with sulphate, hydrochlorate, or nitrate of ammonia, especially when heated. (*Comp.* Wittstein, *Repert.* 57, 62; who, however, explains the reaction in a different way.)

The preparation long known by the name of *Mercurius cinereus Blackii s. Edinburgensium*, obtained by precipitating mercurous nitrate with carbonate of ammonia, is, when prepared with an equal degree of care, almost identical with Hahnemann's quicksilver, but gives off a small quantity of carbonic acid when treated with acids; if, on the contrary, the precipitation be carelessly performed, the product is of a pale grey colour, and probably consists of a mixture of Hahnemann's quicksilver with mercury and nitrate of mercuric oxide and ammonia.

*b. Monobasic.*—By evaporating a mixture of mercurous nitrate and nitrate of ammonia, prismatic crystals are obtained, the aqueous solution of which yields a grey precipitate both with ammonia and with carbonate of potash. (Pagenstecher, *Repert.* 14, 188.) This grey precipitate, as it yields globules of mercury when triturated after drying, and is not turned white by acetic acid, must be regarded as a mixture of metallic mercury and basic nitrate of mercuric oxide and ammonia, inasmuch as the mercurous oxide, at the very moment of precipitation, is resolved into mercuric oxide and metal. (Pagenstecher.) Buchner (*Repert.* 27, 41) in preparing Hahnemann's quicksilver, and leaving the solution to stand over-night, after the addition of a small quantity of ammonia, probably obtained the same salt in small, translucent, bluish-grey, oblique rhombic prisms, having the metallic lustre, and yielding a white powder. These crystals were insoluble [slightly soluble?] in water, but soluble in nitric acid, gave off nitric acid when heated with oil of vitriol, and were blackened by potash, but did not give off ammonia. From these properties, Buchner was led to regard them as basic nitrate of mercurous oxide. According to C. G. Mitscherlich, however, the crystals give off ammonia much more freely with sulphide of barium than with potash; and crystals obtained by that chemist under similar circumstances yielded white calomel when triturated with common salt; they could not, therefore, be a basic salt.

II. Compounds of Basic Mercuric Nitrate with Mercuric Amide.—*a.* $Hg,NH^2+5HgO,NO^5$?—Sometimes obtained in the form of a yellow precipitate when a strong solution of mercuric nitrate is mixed with a very large excess of ammonia. Frequently, however, the salt *b* or *c* is formed instead of this compound. Contains 84 or 85 per cent. of mercury, together with mononitrate of ammonia. (Kane, *Ann. Chim. Phys.* 72, 242.)

To this head probably belongs one of the three salts examined by Pagenstecher (*Repert.* 27, 1), and formed by mixing a solution of mercuric

(or mercurous) nitrate with a large excess of ammonia, and leaving the liquid to evaporate; the salt is then precipitated. It is light yellow, but gradually turns brown when exposed to sunlight. When decomposed by sulphuretted hydrogen under water, it yields a neutral solution of nitrate of ammonia, containing 6·08 per cent., and 96·5 per cent. of sulphide of mercury (= 83·18 metal = 89·84 mercuric oxide). When heated in a retort, it gives off nitrous fumes, together with a small quantity of water; forms a yellowish-red sublimate; and leaves a red powder, which disappears on the application of a strong heat, and yields an orange-yellow sublimate, quite free from metallic mercury. Dissolves in cold hydrochloric acid, and is precipitated unchanged by ammonia; dissolves sparingly in ammonia; and crystallizes out as the ammonia evaporates. Not decomposed by oil of vitriol, or by warm aqueous potash; the latter, however, deepens the yellow colour. (Pagenstecher.)

*b*. $Hg,NH^2 + 3HgO,NO^5$.—1. Formed by decomposing a dilute solution of mercuric nitrate with a slight excess of ammonia. (Soubeiran.) The precipitation must be performed at a high temperature, or, if the precipitate be formed in the cold, the mixture must be afterwards heated. The same compound is formed on boiling the salt *c* with water.

White granular powder, which, when heated, turns yellow, gives off nitrogen gas, ammonia, and afterwards nitrous fumes, and finally oxygen gas and mercury. (Kane.) When suspended in water through which a current of suphuretted hydrogen is passed, it yields sulphide of mercury and a neutral solution of nitrate of ammonia. (Soubeiran, Kane.) Boiled with hydrochloric acid, it gives off nitrous fumes. Dissolves in cold hydrochloric acid, and is precipitated from the solution in the form of a granular powder by water; dissolves very sparingly and without decomposition in nitric and sulphuric acid; dissolves in ammonia and is partly precipitated from the solution by water. (Soubeiran.) Not dissolved or decomposed by water or solution of potash, either cold or boiling. (Soubeiran.)

| | | | Kane. | | Soubeiran. |
|---|---|---|---|---|---|
| $4Hg$ | 400 | 80·97 | 81·26 | | 79·8 |
| $NH^2$ | 16 | 3·24 | | | |
| $3O$ | 24 | 4·86 | | | |
| $NO^5$ | 54 | 10·93 | | | |
| | 494 | 100·00 | | | |

May likewise be regarded as $Hg^3N + HgO,NO^5 + 2HO$. (Rammelsberg.)

*c*. $Hg,NH^2 + 2HgO,NO^5$.—Formed by precipitating a dilute solution of mercuric nitrate containing the slightest possible excess of acid, with dilute ammonia, not in excess. The same compound is likewise formed when terbasic nitrate of mercuric oxide is boiled for a moment with solution of nitrate of ammonia, which thereby acquires an acid reaction :

$$(3HgO,NO^5 + HO) + NH^3,NO^5 = (Hg,NH^2 + 2HgO,NO^5) + NO^5 + 2HO.$$

Soft, white precipitate, which remains for a long time suspended in the liquid, and may be dried at 100° without decomposition. Exhibits the same characters as *b*, when heated, or when acted upon by potash. Boiled with water, it gives up a small quantity of nitrate of ammonia and is converted into the salt *b*, becoming thereby granular and of a less pure white. (Kane.) Dissolves sparingly in aqueous nitrate of ammonia containing free ammonia. (C. G. Mitscherlich.)

| | | | Kane. | C. G. Mitscherlich. | | Pagenstecher. |
|---|---|---|---|---|---|---|
| 3Hg | 300 | 77·72 | 76·41 | 75·47 | | 74·12 |
| $NH^2$ | 16 | 4·15 | 3·78 | 4·40 | | |
| 2O | 16 | 4·15 | | 6·05 | | 5·92 |
| $NO^5$ | 54 | 13·98 | 12·66 | 14·33 | $NH^4O,NO^5$ | 17·40 |
| | 386 | 100·00 | | 100·25 | | |

*d.* $Hg,NH^2+3HgO,NO^5+NH^4O,NO^5$, according to Kane, or $2HgO+NH^3,NO^5$, according to C. G. Mitscherlich.—The salt *c* dissolved in aqueous nitrate of ammonia, yields yellowish crystals on evaporation. J. C. Fr. Meyer likewise obtained crystals united in stellate masses, by supersaturating mercuric nitrate with caustic ammonia or carbonate of ammonia, till the precipitate was redissolved, and then evaporating the liquid.—The crystals are easily decomposed by alkaline hydrosulphates and by hydrochloric acid, but not by other acids. Nitric acid dissolves them very sparingly; sulphuric acid, ammonia, and potash, have no action upon them; baryta-water decomposes the salt but very imperfectly and with great difficulty. (C. G. Mitscherlich.)

To this head perhaps should also be assigned Pagenstecher's salt, which separates after a few hours from a mixture of mercuric nitrate and nitrate of ammonia, and is likewise produced by digesting mercuric oxide, at a gentle heat with a strong solution of nitrate of ammonia. It is white; does not turn brown when exposed to light; gives off more water by distillation than *c;* and nevertheless evolves ammonia when treated with potash, and acid vapours with oil of vitriol. (Pagenstecher.)—Mercuric nitrate forms a white precipitate with nitrate of ammonia; the liquid filtered from this precipitate yields, on evaporation, six-sided prisms with pyramidal summits. (Fourcroy, *Ann. Chim.* 14, 37.)

| | | | C. G. Mitscherlich. | | Pagenstecher. |
|---|---|---|---|---|---|
| 2HgO | 216 | 75·26 | 75·22 | | 73·50 |
| $NH^3$ | 17 | 5·92 | 5·80 | } | 23·75 |
| $NO^5$ | 54 | 18·82 | 18·12 | } | |
| | 287 | 100·00 | 99·14 | | |

*e.* $Hg,NH^2+3HgO,NO^5+2(NH^4O,NO^5)+2HO$, or $4HgO+3(NH^4O,NO^5)$.—The solution of the salt *c* in a strong boiling solution of nitrate of ammonia, filtered hot, yields, on cooling, shining needles which after a while become dull and opaque.—Water extracts nitrate of ammonia from these crystals, and leaves the salt *c.*—The same salt is obtained by boiling mercuric nitrate with nitrate of ammonia. (Kane, *Ann. Chim. Phys.* 72, 242.)

| | | | Kane. |
|---|---|---|---|
| 4Hg | 400 | 59·52 | 58·79 |
| 4O | 32 | 4·76 | |
| $3NH^3$ | 51 | 7·59 | 7·65 |
| $3NO^5$ | 162 | 24·11 | 24·70 |
| 3HO | 27 | 4·02 | |
| | 672 | 100·00 | |

Mercuric oxide dissolves in a very large excess of nitrate of ammonia, forming a liquid which is not precipitated by ammonia; so likewise does mercurous oxide, but with separation of metallic mercury. (Wittstein, *Repert.* 57, 70.)

*Soubeiran's so-called Mercurous salt, Protonitrate ammoniaco-mercuriel.*—Formed by mixing a solution of mercurous nitrate with a large

quantity of nitric acid or nitrate of ammonia, and then precipitating by ammonia; or by adding ammonia to the solution of mercurous nitrate till the precipitate begins to turn white, then filtering and precipitating by ammonia.—White, tasteless powder. Heated in a glass tube, it gives off nitrous fumes, sometimes with emission of light, and leaves red oxide of mercury. When suspended in water, through which sulphuretted hydrogen is passed, it is resolved into 95·87 per cent. of sulphide of mercury and a neutral solution of nitrate of ammonia. It dissolves abundantly in hot oil of vitriol, which decomposes it but slightly. Nitric acid dissolves it without decomposition, and the more abundantly, the hotter it is. It dissolves slowly in cold, more quickly in hot hydrochloric acid.—Aqueous ammonia dissolves it in considerable quantity. It is not dissolved or altered, even at a boiling heat, by water, or by a strong solution of potash or soda.—Contains 92·2 per cent. (4 At.) mercurous oxide, 1·88 p. c. (1 At.) of ammonia, and 5·92 p. c. (1 At.) of nitric acid. (Soubeiran, *J. Pharm.* 12, 465, 509 and 561; also *N. Tr.* 14, 1, 197; further, *Ann. Chim. Phys.* 36, 220.)—This view of its composition appears to be confirmed by its formation from a solution of mercurous oxide. It must not be forgotten, however, that such a solution often contains mercuric oxide. This oxide is likewise formed from the mercurous oxide, with separation of metallic mercury, by the action of ammonia and nitrate of ammonia, which latter is added by Soubeiran to the mercury solution, either in the form of the salt or of its separate constituents. (That such decomposition of the mercurous oxide may take place, is shown, both by the facts adduced on page 91, and by the following experiments of C. G. Mitscherlich.) Mercurous oxide is quickly decomposed in a strong solution of nitrate of ammonia, and slowly in a dilute solution, into metallic mercury and a white mercuric double salt. On adding ammonia to a mercurial solution previously mixed with nitrate of ammonia, metallic mercury is precipitated, and the filtrate treated with potash yields a white mercuric double salt.— It is true that Soubeiran found that the sulphide of mercury thrown down from the solution by hydrosulphuric acid yielded globules of mercury on trituration, and 92 per cent. of mercury globules when distilled with lime, and consequently had the composition of disulphide of mercury; but this result might perhaps be due to the presence of metallic mercury in the preparation used for the experiment. On the other hand, the solubility of the salt in hydrochloric acid, without separation of calomel, a property first recognized by Soubeiran himself, is in favour of the supposition that it is a mercuric salt. Moreover, Pagenstecher, C. G. Mitscherlich, and Kane were unable to form any white mercurous salt agreeing with this compound.—Hence it is probable that Soubeiran's salt is the mercuric salt *b*, partly mixed with mercury.

## Mercury and Potassium.

A. Potassium-amalgam.—1. The two metals unite even at ordinary temperatures, the combination being attended with great evolution of heat. (H. Davy.)—2. When mercury is placed in a cup connected with the negative pole of a voltaic battery of at least 20 pairs, and covered with a strong solution of potash in which a piece of hydrate of potash is immersed, and into which the positive wire dips, the mercury takes up potassium.

(Berzelius.) 1 part of potassium forms with 30 parts of mercury, an amalgam which, after cooling, is tolerably hard and brittle; with 70 pts. mercury it likewise forms an amalgam which is solid at ordinary temperatures, but with more than 70 pts., it forms a liquid amalgam. (H. Davy.) According to Gay-Lussac and Thénard, the amalgam is solid and crystalline when it contains from 70 to 96 pts. of mercury to 1 pt. of potassium, but liquid when the proportion of mercury amounts to 140. According to Böttger (*J. pr. Chem.* 1, 303), the amalgam is perfectly solid when it contains 100 pts. of mercury to 1 pt. of potassium; with 140 mercury, it is very hard; with 180 mercury, friable and partially crystallized; with 200 mercury, viscid. The amalgam crystallizes in cubes. (Berzelius & Pontin.) The solid amalgam fuses when slightly heated. It gives off its mercury below a red heat. (H. Davy.) When exposed to the air or immersed in water, it is resolved into mercury and aqueous potash, hydrogen gas being slowly evolved; a similar change is produced by aqueous acids. In contact with moist ammoniacal salts, it is resolved into a potash-salt and ammoniacal amalgam. It amalgamates easily with iron and platinum. (H. Davy.)

Mercuric oxide is slightly soluble in aqueous carbonate of potash. (Berzelius, Wittstein, *Repert.* 81, 156.)

B. Sulphide of Mercury and Potassium; hydrated.—When cinnabar is prepared in the humid way by Kirchhoff's process (p. 22), the liquid separated from the cinnabar contains a considerable quantity of mercury in solution, in consequence of the large excess of potash present, and, when evaporated in a retort, and subsequently cooled, yields at first crystals of hyposulphite of potash, and then, after further concentration, solidifies in a gelatinous mass, consisting of very fine silky needles. These needles are dried by pressure, between blotting-paper. When exposed to the air, they soon turn grey and afterwards black, emitting an odour like that of sulphuretted hydrogen, with which another odour is mixed. Under water they resolve themselves into a black powder, of which a larger quantity separates from the liquid on further dilution; but if the water contains sal-ammoniac, the whole of the black powder separates immediately. This black powder has the characters of black sulphide of mercury, but contains a few globules of mercury; the aqueous liquid is free from mercury, and contains sulphide of potassium together with hyposulphite of potash. This salt cannot be prepared by treating cinnabar with aqueous hyposulphite of potash and sulphide of potassium. (Brunner, *Pogg.* 15, 596.)

| | *Crystallized.* | | | | Brunner. |
|---|---|---|---|---|---|
| K | 39·2 | .... | 18·13 | .... | 18·26 |
| S | 16·0 | .... | 7·40 | .... | 7·08 |
| Hg | 100·0 | .... | 46·25 | } | 54·28 |
| S | 16·0 | .... | 7·40 | } | |
| 5HO | 45·0 | .... | 20·82 | | |
| KS,HgS+5Aq. | 216·2 | .... | 100·00 | | |

C. Hyposulphite of Mercuric Oxide and Potash.—Formed by agitating a solution of 5 pts. hyposulphite of potash in 24 pts. of boiling water with 2 pts. finely pounded mercuric oxide, warming the liquid frequently till the oxide is completely dissolved, and filtering hot. (Kirchhoff.) Mercuric oxide dissolves, with evolution of heat, in hyposulphite of potash; when mercurous oxide is used, metallic mercury remains undissolved. The liquid must not be boiled, otherwise black sulphide of

mercury will separate out. (Rammelsberg.) The solution, as it cools, deposits delicate white prisms, which must be separated from the mother-liquid, containing free potash, washed with cold water, and again crystallized from solution in hot water. They then no longer redden turmeric; their taste is bitter and afterwards metallic. (Kirchhoff.) The crystals have the form of *fig.* 55. (Herschel.)

| | *Crystallized.* | | | Rammelsberg. | | Kirchhoff. |
|---|---|---|---|---|---|---|
| KO ..... | 47·2 | .... | 18·79 | ..... | 24·75 | .... 23·81 |
| HgO ..... | 108·0 | .... | 42·99 | ..... | 33·18 | .... 42·83 |
| $2S^2O^2$ ..... | 96·0 | .... | 38·22 | ..... | 41·27 | .... |
| $KO,S^2O^2+HgO,S^2O^2$ | 251·2 | .... | 100·00 | ..... | 99·20 | |

The salt becomes somewhat grey on drying. (Kirchhoff.) Turns black when exposed to light. (Rammelsberg.) Does not effloresce in the air. (Kirchhoff.) When distilled alone, it gives off sulphurous acid, sulphur, sulphide of mercury, and metallic mercury, and leaves sulphate of potash (Rammelsberg), amounting to 44 per cent. (Kirchhoff.) When distilled with water, it yields a distillate containing sulphurous acid, whilst 46 per cent. of cinnabar remains in the retort, together with a slight excess of sulphur and sulphate of potash. (Kirchhoff.) The aqueous solution deposits black sulphide of mercury on boiling, and cinnabar when left at rest. (Rammelsberg.) Sulphuric, hydrochloric, and nitric acid, render the solution milky in the course of five minutes (from separation of sulphur, according to Rammelsberg), and throw down cinnabar, causing at the same time an evolution of sulphurous acid gas. The solution is not affected by sulphurous acid, acetic acid, potash, or soda. Baryta or lime-water produces, after a while, a greyish yellow precipitate, which gives off sulphurous acid when treated with stronger acids. Mercurous nitrate produces a blackish grey precipitate; bismuth, lead, iron, and copper, decompose the salt. (Kirchhoff.) Lead-salts produce a white precipitate; silver-salts, a precipitate which contains mercury, and is yellow at first, but afterwards turns brown. (Rammelsberg, *Pogg.* 56, 315.) The salts of baryta, zinc-oxide, cadmic oxide, and ferrous oxide, produce no precipitate. This salt is soluble in 10 parts of water at 15°, and in half its weight of boiling water; alcohol precipitates it from the aqueous solution. (Kirchhoff, *Scher. Ann.* 2, 30.)

¶. C′. Sulphate of Mercuric Oxide and Potash.—$KO,SO^3 + 3(HgO,SO^3) + 2$ Aq.—Prepared by dissolving 1 At. anhydrous mercuric sulphate in hot sulphuric acid, digesting the liquid with a solution of 1 At. sulphate of potash till the precipitate first formed re-dissolves, then adding boiling water till a permanent turbidity is produced, and leaving the whole to cool slowly. Large colourless crystals belonging to the oblique prismatic system. (Hirzel, *Zeitschr. f. Pharm.* 1850, 17.) ¶

D. Iodide of Mercury and Potassium.—a. *Mono-acid?*—KI, HgI.—This salt may be supposed to exist in the liquid obtained by dissolving the salt *b* in water, inasmuch as 1 atom of mercuric iodide is thereby separated. The solution, when evaporated, yields no crystals, but a yellowish mass; and on dissolving this mass in water, iodide of potassium separates out at first, but is re-dissolved on agitation. (P. Boullay, *Ann. Chim. Phys.* 34, 345.) This liquid must be regarded as a solution of the salt *b* in aqueous iodide of potassium; for when evaporated, it yields needles of the salt *b* and cubes of iodide of potassium. (Souville, *J. Pharm.* 26, 475; Labouré, *N. J. Pharm.* 4, 300.)

*b. Bi-acid.* — KI,2HgI. — 1. Formed by saturating hot aqueous iodide of potassium with protiodide of mercury; leaving the solution to cool till the third atom of mercuric iodide has crystallized out; then pouring off the liquid, and leaving it to cool to a still lower temperature: prisms of the salt *b* are then obtained. (Boullay.) Aqueous iodide of potassium saturated in the cold with mercuric iodide, and then evaporated in the open air, if it be very dry, or else under a bell-jar over oil of vitriol, likewise yields the crystals. (v. Bonsdorff). — 2. The double salt may also be obtained by saturating a boiling solution of potash with iodide of mercury, whereupon mercuric oxide separates out; as the liquid cools, iodide of mercury is first deposited, and afterwards the salt *b*.

$$4HgI + KO = (KI,3HgI) + HgO.$$

Also when iodide of mercury is boiled with alcoholic potash, or with carbonate of potash and alcohol, a liquid is obtained, which, on cooling, deposits yellow needles of the salt *b*. (Berthemot, *J. Pharm.* 14, 186.)— 2. By boiling either the protoxide or the dioxide of mercuric oxide with aqueous iodide of potassium, the protoxide is completely dissolved, and the liquid contains free potash, with only 2 At. iodide of mercury to 1 At. iodide of potassium, and therefore, on cooling, deposits no iodide of mercury, but only the salt *b*; when the dioxide is used, metallic mercury immediately separates, mixed, if the oxide is in excess, with diniodide of mercury (Berthemot):

$$2HgO,3KI = KI,2HgI + 2KO.$$

4. By evaporating the solution of corrosive sublimate in aqueous iodide of potassium till it crystallizes, and dissolving out the salt *b* with alcohol, which leaves behind the chloride of potassium. (Bonsdorff, *Pogg.* 17, 265):

$$2HgCl + 3KI = KI,2HgI + 2KCl.$$

Long, yellow prisms, resembling the ammonium-compound and sulphur; somewhat greenish after drying. Gives off a small quantity of water when heated, afterwards fuses to a red liquid, and lastly gives off iodide of mercury. (Boullay.) The liquid obtained by the application of a moderate heat is oily and yellow, and, on cooling, solidifies in a greenish yellow mass, having a radiating fracture; but at a higher temperature, it turns brown, and afterwards solidifies, on cooling, in a mass having a granular fracture; at a still higher temperature, it turns dark brown, and gives off iodide of mercury. (Brandes & Böhm, *N. Br. Arch.* 23, 175.)— The salt, when heated with copper or iron, gives up all its mercury, which distils over. Chlorine gas decomposes it, and on the application of heat, finally converts it into chloride of potassium. Dilute acids separate all the iodide of mercury from it. Water separates about half the iodide of mercury, and forms a solution containing the salt *a*. (Boullay.) The salt is permanent in dry air, but becomes moist in air which is not quite dry. When a stratum of its alcoholic solution is left to evaporate in a watch-glass, so that a thin film of the salt may remain on the glass, this residue turns red when breathed upon, but recovers its yellow colour on being gently heated. (Brandes & Böhm.) Strong acetic acid (which neither dissolves iodide of potassium nor iodide of mercury) dissolves the double salt, and water added to the solution separates iodide of mercury. (Berthemot.) The salt dissolves without decomposition in strong alcohol and in ether. (Boullay, Berthemot.) The alcoholic solution may be mixed with the ethereal solution without producing a precipitate. The solution

in alcohol of 70 per cent., or weaker, deposits beautiful crystals of iodide of mercury, when left to evaporate spontaneously. (Brandes & Böhm.)

| | *Anhydrous.* | | | Boullay. |
|---|---|---|---|---|
| KI | 165·2 | .... | 26·77 | .... 29·7 |
| 2HgI | 452·0 | .... | 73·23 | .... 70·3 |
| KI,2HgI | 617·2 | .... | 100·00 | .... 100·0 |

| | *Crystallized.* | | | Boullay. |
|---|---|---|---|---|
| KI,2HgI | 617·2 | .... | 95·81 | .... 95·5 |
| 3HO | 27·0 | .... | 4·19 | .... 4·5 |
| +3Aq. | 644·2 | .... | 100·00 | .... 100.0 |

*c. Ter-acid ?*—165·2 pts. (1 At.) of iodide of potassium, dissolved in a small quantity of water, take up 672 pts. (3 At.) of iodide of mercury at a boiling heat, but the solution deposits 1 At. again on cooling. On the addition of alcohol, a smaller quantity of mercuric iodide separates out. (Boullay.) According to Souville, a boiling aqueous solution of iodide of potassium dissolves more than 2 atoms of mercuric iodide, but not so much as 3 atoms; the mixture, therefore, is not a definite compound, but a mere solution of mercuric iodide in the solution of salt *b*.

Iodide of potassium dissolved in a boiling solution of mercuric nitrate, yields, on cooling, flat, colourless needles, consisting of a compound of iodide of potassium with mercuric nitrate; they are easily decomposed by water, and when heated, give off iodide of mercury, together with the decomposition-products of nitric acid. (Preuss, *Ann. Pharm.* 29, 328.)

E. Bromide of Mercury and Potassium. — *a. Mono-acid ?*—The aqueous solution of equal parts of bromide of potassium and salt *b*, yields on evaporation, prismatic crystals, which are permanent in the air, and probably consist of KBr,HgBr.—(Bonsdorff, *Pogg.* 19, 339.)

*b. Bi-acid.*—Formed by saturating a moderately concentrated solution of bromide of potassium with protobromide of mercury, and evaporating to the crystallizing point. (Löwig, Bonsdorff.)

Yellow octohedrons (Löwig); flattened rhombic prisms with the terminal faces somewhat oblique. (Bonsdorff.) Löwig's salt was anhydrous, Bonsdorff's contained water. The crystals fuse without giving off water, and yield a sublimate of mercuric bromide. Considerable quantities of water separate half the mercuric bromide. (Löwig.) A concentrated solution of bromide of potassium takes up about 3 At. bromide of mercury when heated, and is converted into a stiff, opaque mass, which, when cooled or diluted with water, gives up the excess of bromide of mercury, so that only 2 At. remain in solution. (Löwig.)

| | | *Anhydrous.* | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|---|
| KBr | 117·6 | .... | 24·79 | KBr | 117·6 | .... | 23·88 | .... 24·10 |
| 2HgBr | 356·8 | .... | 75·21 | 2HgBr | 356·8 | .... | 72·46 | .... 72·42 |
| | | | | 2HO | 18·0 | .... | 3·66 | .... 3·48 |
| KBr,2HgBr | 474·4 | .... | 100·00 | +2Aq.. | 492·4 | .... | 100·00 | .... 100·00 |

F. Chloride of Mercury and Potassium. — *a. Mono-acid.* — A solution of 7 pts. chloride of potassium in 21 pts. water, moderately heated, takes up 8 pts. of corrosive sublimate; afterwards, if cooled down to 15·5, it deposits a few needles; and at 10°, solidifies almost completely in a mass composed of needles. (J. Davy.)—1. An aqueous solution of chloride of calcium mixed with a solution of corrosive sublimate in excess,

deposits, on the addition of alcohol, a quantity of silky needles united in tufts. (Liebig, *Schw.* 49, 252.)—2. The compound is also formed by adding to the aqueous solution of salt *b*, as much chloride of potassium as it already contains, and leaving the mixture to evaporate in the air. Cubes of chloride of potassium separate out at the last. (Bonsdorff, *Pogg.* 17, 123.)

Large, colourless, right rhombic prisms. *Fig.* 62. $u' : u = 110°$; $u : a = 141° 30'$; $p : a = 123° 30'$.—The chloride of mercury in this and the following salts can only be separated by continued ignition in an open vessel. This salt is easily soluble in water, sparingly in alcohol.

| | *Anhydrous.* | | | | Liebig. |
|---|---|---|---|---|---|
| KCl | 74·6 | .... | 35·52 | .... | 35·32 |
| HgCl | 135·4 | .... | 64 48 | .... | 64·68 |
| KCl,HgCl | 210·0 | .... | 100·00 | .... | 100·00 |

| | *Crystallized.* | | | | Bonsdorff. |
|---|---|---|---|---|---|
| KCl | 74·6 | .... | 34·07 | .... | 33·73 |
| HgCl | 135·4 | .... | 61·82 | .... | 61·31 |
| HO | 9·0 | .... | 4·11 | .... | 4·96 |
| KCl,HgCl + Aq | 219·0 | .... | 100·00 | .... | 100·00 |

*b. Bi-acid.*—A solution of chloride of potassium, saturated in the cold, is digested at 30°, with excess of corrosive sublimate, water being continually dropped in and the liquid stirred,—and the solution is filtered warm through a heated funnel, and afterwards left to cool. The filtrate first deposits crystals of salt *c*; afterwards, if decanted from these, and abandoned to spontaneous evaporation, it yields crystals of salt *b*.—Flattened, four-sided prisms and needles, united in stellate groups, and having their terminal faces inclined at an angle of 92°....93°, to the lateral faces. They dissolve easily in water, sparingly in alcohol. (Bonsdorff, *Pogg.* 19, 336.) The same compound is obtained in silky needles, by dissolving in water the crystals which separate from a solution of corrosive sublimate in cold concentrated hydrochloric acid, and saturating the acid with potash. (Boullay, *Ann. Chim. Phys.* 34, 344.)

| | *Anhydrous.* | | |
|---|---|---|---|
| KCl | 74·6 | .... | 21·6 |
| 2HgCl | 270·8 | .... | 78·4 |
| KCl,2HgCl | 345·4 | .... | 100·0 |

| | *Crystallized.* | | | | Bonsdorff. |
|---|---|---|---|---|---|
| KCl | 74·6 | .... | 20·53 | .... | 20·97 |
| 2HgCl | 270·8 | .... | 74·52 | .... | 75·24 |
| 2HO | 18·0 | .... | 4·95 | .... | 3·79 |
| KCl,2HgCl + 2Aq. | 363·4 | .... | 100·00 | .... | 100·00 |

*c. Quadracid.*—1. Formed by agitating a saturated aqueous solution of chloride of potassium, at a temperature between 50° and 60°, with pulverized corrosive sublimate. On cooling, the liquid solidifies in an asbestos-like mass, consisting of fine silky needles. (Bonsdorff, *Pogg.* 17, 122.)—2. When boiling hydrochloric acid is saturated with corrosive sublimate, and the solution neutralized with potash and left to cool, silky needles of the salt *c* are obtained. (Boullay.)

The needles are rhombic prisms with angles of about 112° and 68°. They dissolve very easily in warm water; a solution which still remains

clear at 18° may deposit an abundance of needles at 15°; the liquid is very apt to effloresce during evaporation. The salt is sparingly dissolved by alcohol. (Bonsdorff.)

| | *Anhydrous.* | | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|---|
| KCl | 74·6 | .... | 12·11 | KCl | 74·6 | .... | 11·46 | .... 11·34 |
| 4HgCl | 541·6 | .... | 87·89 | 4HgCl | 541·6 | .... | 83·04 | .... 83·10 |
| | | | | 4HO | 36·0 | .... | 5·50 | .... 5·56 |
| KCl,4HgCl | 616·2 | .... | 100·00 | +4Aq | 652·2 | .... | 100·00 | .... 100·00 |

The solution of the salt *c* in water dissolves an additional quantity of corrosive sublimate at a boiling heat, and on cooling, or on the addition of a small quantity of water, deposits it again in needles, after which the salt *c* crystallizes out. (Bonsdorff.)

## Mercury and Sodium.

A. Sodium-amalgam.—Sodium combines rapidly with mercury at ordinary temperatures, the combination being attended with a hissing noise and vivid combustion. (Gay-Lussac & Thénard, *Recherches*, 1, 246.) A piece of sodium forcibly thrown upon mercury, is thrown out of the vessel with explosion, in consequence of the great heat produced. (Serullas, *Ann. Chim. Phys.* 40, 328.) To form the amalgam, the two metals should be triturated together in a dry mortar fitted with a cover, and the mixture immersed in rock-oil as soon as the combustion is over. (Böttger.) The amalgam has the colour of mercury. When it contains 30 parts of mercury to 1 part of sodium, it is tolerably hard under the file, which wears it away in the form of powder; it exhibits a crystalline, laminar fracture. (Lampadius, *Kastn. Arch.* 16, 102.) When it contains 40 parts of mercury, it is still solid, but softer than with 30 parts. (Lampadius.) An amalgam containing 60 parts of mercury to 1 part of sodium forms a stiff paste at 21°. (Böttger.) 64 parts of mercury and 1 of sodium form a compound which exhibits a confused crystalline structure. (Gay-Lussac & Thénard.) 80 parts mercury to 1 sodium: pasty at 21°. (Böttger.) 86 mercury to 1 sodium: a mass containing numerous small granular crystals. (Gay-Lussac & Thénard.) 100 mercury to 1 sodium: viscid, and consisting of a solid and a liquid portion. (Böttger.) 128 mercury to 1 sodium: liquid. (Gay-Lussac & Thénard.) Sodium-amalgam exhibits the same decompositions as potassium-amalgam. It likewise amalgamates iron and platinum. (H. Davy.) It decomposes the salts of baryta and strontia, and many heavy metallic salts, when a small quantity of water is present, the product being a compound of mercury with the heavy metal. (Böttger, *J. pr. Chem.* 3, 283.)

B. Hyposulphite of Mercuric Oxide and Soda.—Mercuric oxide dissolves quickly in aqueous hyposulphite of soda, setting the soda free. The liquid has a sweet, metallic taste, and becomes turbid when left to itself or when evaporated, even in vacuo, depositing a large quantity of cinnabar. (Herschel, *Edinb. Phil. J.* 2, 154.) Alcohol added to this solution throws down a tenacious mass, which after long standing, deposits black sulphide of mercury; the salt cannot be obtained in the solid state. (Rammelsberg, *Pogg.* 56, 318.)

C. Iodide of Mercury and Sodium.—Aqueous iodide of sodium, saturated in the cold with iodide of mercury and evaporated over oil of vitriol in a bell-jar containing air, yields large, sulphur-yellow, rhombic prisms, with many secondary faces: these crystals deliquesce rapidly when exposed to the air. (Bonsdorff, *Pogg.* 17, 266.)—199·2 pts. (1 At.) of iodide of sodium dissolved in a small quantity of water, take up, when heated, 695 pts. (a little more than 3 At.) of iodide of mercury; the solution, on cooling, deposits a portion of it (probably 1 At.), and when evaporated, yields no crystals, but a yellow mass, from which iodide of mercury is separated even by trituration, or by cooling. If, for example, the inner surface of a basin in which the evaporation has been carried almost to dryness, be scratched with a glass rod, iodide of mercury separates at that part, and thence the separation proceeds throughout the whole mass. If the evaporated mass be dissolved in a large quantity of water, iodide of mercury likewise separates out, probably 1 At., and the filtrate, when very slowly evaporated, yields long, very deliquescent needles. (Boullay.) This salt is likewise obtained by boiling iodide of mercury with aqueous or alcoholic soda, or with carbonate of soda and alcohol, or by boiling mercuric or mercurous oxide with aqueous iodide of sodium. It is not crystalline; deliquesces very quickly. (Berthemot.)

D. Bromide of Mercury and Sodium.—Sometimes in needles, sometimes in tolerably large rhombic prisms; deliquescent in the air. (Bonsdorff.)

E. Chloride of Mercury and Sodium. A solution of 7 pts. common salt in 20 pts. water, takes up 32 pts. corrosive sublimate at 15·5°, and 3 pts. more when gently heated; it then has a specific gravity of 2·14, and is in a condition to take up a little more common salt; the whole remains dissolved when the liquid cools. If, on the contrary, a still larger quantity of corrosive sublimate be dissolved at a higher temperature in the saturated solution of common salt, small rhomboidal crystals are formed on cooling. (J. Davy.) The mono-acid salt cannot be obtained in the crystalline form. (Bonsdorff.) — *Bi-acid salt.*—1. Formed by agitating a saturated solution of common salt with corrosive sublimate, as long as any of the latter is dissolved, and leaving the filtrate to evaporate spontaneously. (Bonsdorff.)—2. A solution of equal parts of common salt and corrosive sublimate abandoned to spontaneous evaporation, first yields crystals of common salt, and afterwards long needles of the double salt. (Schindler, *Repert.* 36, 240.)— Irregular six-sided needles, united in tufts; permanent in the air. (Bonsdorff.) — The crystals fuse in their water of crystallization at 100°, and when more strongly heated, boil up and give off this water, together with a small quantity of chloride of mercury.—They dissolve in 0·33 pts. water at 150°; their solution exhibits with alkalis the same precipitations as a solution of corrosive sublimate, and gives a white precipitate with spring-water containing carbonate of lime. (Schindler.) When the aqueous solution is agitated with ether, the latter dissolves out, not the corrosive sublimate alone, but the undecomposed double salt, and the solution contains 1 part of that salt in 275 parts of ether. (Lassaigne, *Ann. Chim. Phys.* 64, 104.)

| | *Anhydrous.* | | |
|---|---|---|---|
| NaCl | 58·6 | .... | 17·79 |
| 2HgCl | 270·8 | .... | 82·21 |
| NaCl,2HgCl | 329·4 | .... | 100·00 |

| | *Crystallized.* | | Bonsdorff. | Schindler. |
|---|---|---|---|---|
| NaCl | 58·6 | 16·44 | 16·0 | 16·10 |
| 2HgCl | 270·8 | 75·98 | 75·0 | 75·86 |
| 3HO | 27·0 | 7·58 | 8·8 | 7·73 |
| NaC,2HgCl + 3Aq. | 356·4 | 100·00 | 99·8 | 99·69 |

F. Amalgam of Potassium and Sodium.—A mixture of equal parts of potassium and sodium agitated with mercury, combines with it, producing a remarkably vivid incandescence. (Accum.) An alloy of 1 pt. sodium, 10 potassium, and 200 mercury, solidifies in an extremely solid mass. (Böttger, *J. pr. Chem.* 1, 303.)

## Mercury and Lithium.

A. Lithium-amalgam.—Formed, when the negative pole of a voltaic battery is placed in contact with mercury covered with a strong aqueous solution of lithia, into which the positive wire dips. (Mitscherlich, *Lehrb.* 2, 84.)

B. Chloride of Mercury and Lithium.—There are two double chlorides of this nature, one of which crystallizes in needles, which are permanent in the air, while the other is deliquescent. (Bonsdorff.)

## Mercury and Barium.

A. Barium-amalgam.—Obtained by the galvanic process (I, 458; III, 133). H. Davy. This amalgam has very little fluidity; becomes covered with a grey film on exposure to the air, and decomposes slowly in pure water; more quickly in water containing sulphuric acid. (Berzelius & Pontin.)—2. Sodium-amalgam containing 100 parts of mercury to 1 part of sodium, when immersed in a saturated solution of chloride of barium, is converted, with very feeble evolution of gas, into barium-amalgam. The latter is taken out of the liquid as soon as the stronger evolution of gas ceases, then dried between bibulous paper, and immersed in rock-oil. The amalgam thus prepared has about one and a half times the volume of the sodium-amalgam used; it is solid, rough, uneven, and may be reduced by pressure between the fingers to a sandy paste. When exposed to the air for some time, it is converted into mercury and carbonate of baryta. When immersed in water, it gives off hydrogen gas, and forms baryta-water. In a saturated solution of sal-ammoniac it forms a tolerably bulky ammoniacal amalgam. In a saturated solution of blue vitriol, the globule of amalgam immediately begins to rotate, causing the solution to move in two opposite directions, and at the same time sulphate of baryta shoots out in flakes, which assume various hues, from the presence of cuprous oxide and hydrated cupric oxide, and look like a growth of moss; the action goes on for 15 or 20 minutes, by which time the whole of the barium is converted into sulphate. (Böttger, *J. pr. Chem.* 1, 305.)

B. Sulphide of Mercury and Barium.—Black sulphide of mercury is slightly soluble in aqueous sulphide of barium. (Rammelsberg, *Pogg.* 48, 176.)

C. Hyposulphite of Mercuric Oxide and Baryta.—Aqueous hyposulphite of baryta dissolves mercuric oxide, forming an easily decomposible liquid, which does not deposit crystals. (Rammelsberg, *Pogg.* 56, 318.)

D. Iodide of Mercury and Barium.—a. *Mono-acid?*—An aqueous solution of iodide of mercury in aqueous iodide of barium, freed by cooling and dilution from excess of iodide of mercury, yields yellowish crystals, soluble in water.

b. *Bi-acid?*—An aqueous solution of iodide of barium, saturated hot with iodide of mercury, deposits part of the latter on cooling; and when separated therefrom and evaporated, yields crystals which probably contain 2 At. iodide of mercury to 1 At. iodide of barium, and from which the iodide of mercury separates, both when they are dried by heat and when they are dissolved in a larger quantity of water. (P. Boullay.)

E. Bromide of Mercury and Barium.—Prisms having a strong lustre, and deliquescing in the air. (Bonsdorff.)

F. Chloride of Mercury and Barium.—20 parts of water saturated with 8·7 parts of crystallized chloride of barium, dissolve 16 parts of corrosive sublimate at 15°, and 4 parts more when moderately heated. The solution has a specific gravity of 1·9, and, on cooling, deposits a small number of crystals, which appear to have a cubical form. (J. Davy, *Phil. Trans.* 1822, 364.) When an aqueous solution of chloride of barium, saturated in the cold, is agitated with pulverized corrosive sublimate, then filtered, and left to evaporate spontaneously, crystals of corrosive sublimate are first deposited, then the crystals of the double chloride, first in rays and laminæ, united as in Prehnite, afterwards in small tables, having the form of oblique rhombic prisms, whose lateral dihedral angles are equal to 95° and 85°. The crystals effloresce in dry air, but are otherwise permanent in the air. (Bonsdorff, *Pogg.* 17, 130.)

| | *Anhydrous.* | | |
|---|---|---|---|
| BaCl ..... | 104·0 | .... | 27·75 |
| 2HgCl..... | 270·8 | .... | 72·25 |
| BaCl,2HgCl ..... | 374·8 | .... | 100·00 |

| | *Crystallized.* | | | | Bonsdorff. *Rays.* | | Bonsdorff. *Tables.* | |
|---|---|---|---|---|---|---|---|---|
| BaCl..... | 104·0 | .... | 26·48 | .... | 29·49 | .... | 28·67 | |
| 2HgCl ..... | 270·8 | .... | 68·94 | .... | 64·74 | .... | 65·73 | |
| 2HO ..... | 18·0 | .... | 4·58 | .... | 5·77 | ... | 5·60 | |
| BaCl,2HgCl+2Aq. .... | 392·8 | .... | 100·00 | .... | 100·00 | .... | 100·00 | |

## Mercury and Strontium.

A. Strontium-amalgam.—1. Prepared by the galvanic process. (I, 458; III, 167.) H. Davy.—2. By the same process as for barium-amalgam (2); but the strontium-amalgam must be speedily removed from the solution of chloride of strontium, inasmuch as it decomposes in three minutes when immersed in that liquid. It is somewhat viscid. When exposed to the air for 6 to 10 hours, it is completely resolved into mercury and carbonate of strontia. When immersed in water, it yields hydrogen gas and strontia-water. (Böttger.)

B. Hyposulphite of Mercuric Oxide and Strontia.—Similar to the hyposulphite of mercuric oxide and baryta. (Rammelsberg.)

C. Iodide of Mercury and Strontium.—Strictly analogous to iodide of mercury and barium. (Boullay.) Yellowish crystals, which may be obtained by dissolving iodide of mercury in strontia-water. (Berthemot.)

D. Bromide of Mercury and Strontium.—*a. Mono-acid.*—Crystals soluble in all proportions in water.

*b. Bi-acid.*—1 At. bromide of strontium dissolved in twice its weight of water takes up at 50°, 3 At. of iodide of mercury. The solution, on cooling, deposits 1 At. of bromide of mercury, and when poured off from this deposit and evaporated, yields small crystals, containing 2 At. bromide of mercury and 1 At. bromide of strontium. When this compound is digested in water, bromide of mercury remains undissolved, and the liquid takes up the salt *a*. (Löwig, *Mag. Pharm.* 33, 7.)

E. Chloride of Mercury and Strontium.—Needles, permanent in the air, and easily soluble in water.

## Mercury and Calcium.

A. Calcium-amalgam.—Prepared from hydrate of lime by the galvanic method (I, 458; III, 181). Liquid. When exposed to the air, it becomes covered with a black film, consisting of lime and mercurous oxide [finely divided mercury?]. Under water, it is resolved into mercury, lime-water, and hydrogen gas. Does not amalgamate iron. (Berzelius & Pontin.)—2. By immersing potassium or sodium-amalgam in a strong solution of chloride of calcium. (Klauer, *Ann. Pharm.* 10, 89.)

B. Mercurate of Lime.—Formed by boiling mercuric oxide with lime and water, then straining and evaporating. Yellow, transparent crystals. (Berthollet, *Ann. Chim.* 1, 61.)

C. Hyposulphite of Mercuric Oxide and Lime.—Analogous to the hyposulphite of mercuric oxide and baryta. (Rammelsberg.)

D. Iodide of Mercury and Calcium.—Aqueous iodide of calcium, saturated at a high temperature with iodide of mercury, deposits part of that substance on cooling; the remaining liquid, when evaporated, yields crystals, probably containing 2 At. iodide of mercury with 1 At. iodide of calcium; from these, water separates iodide of mercury, and forms a solution, which leaves a yellow mass on evaporation. (P. Boullay.) By boiling iodide of mercury with lime and alcohol, yellowish needles are obtained. (Berthemot.)

E. Bromide of Mercury and Calcium.—Aqueous bromide of calcium saturated with bromide of mercury, and then evaporated, yields, first (*a*), tetrahedrons and octohedrons, which have a strong lustre, are permanent in the air, decompose when treated with a small quantity of water, but dissolve completely on the application of heat, and crystallize out again on cooling; secondly, on further evaporation (*b*), prisms or

needles, which deliquesce very rapidly even in dry air, and undoubtedly contain a smaller quantity of bromide of mercury.

F. Chloride of Mercury and Calcium.—*a. Bi-acid.*—A saturated aqueous solution of chloride of calcium, saturated in the cold with corrosive sublimate, yields a heavy, oily liquid, which, when evaporated by heat or over sulphuric acid, first yields crystals of the salt *b*, then, on cooling, needles of salt *a*, which, by solution in water and evaporation at 30°, are converted into finer crystals. Large rhombic tables, whose lateral dihedral angles are equal to 110° and 70°; frequently, also, flattened, six-sided prisms. They effloresce when dried over sulphuric acid; but deliquesce rapidly in the open air. According to an approximate analysis, they contain $CaCl,2HgCl + 6Aq$.

*b. Penta-acid.*—1. The salt which crystallizes out first in tetrahedrons and octohedrons.—2. A chloride of calcium solution, not completely saturated with corrosive sublimate, yields, when slowly evaporated at a gentle heat in a dry winter atmosphere, large crystals with a great number of faces, one of the vertical angles of which is equal to 125°, and probably belongs to a cubo-octohedron.—The crystals are transparent, with a strong lustre, and tolerably permanent in the air. In water they turn white and decompose, the water principally dissolving out chloride of calcium; but, on the application of heat, the corrosive sublimate likewise dissolves, and the solution, on cooling, first yields crystals of corrosive sublimate, and then of the salt *b*, whilst a deliquescent salt remains in solution. (Bonsdorff.)

| | *Anhydrous.* | | |
|---|---|---|---|
| CaCl | 55·4 | .... | 7·56 |
| 5HgCl | 677·0 | .... | 92·44 |
| CaCl,5HgCl | 732·4 | .... | 100·00 |

| | *Crystallized.* | | | | Bonsdorff. (1) | | (2) | |
|---|---|---|---|---|---|---|---|---|
| CaCl | 55·4 | .... | 6·89 | .... | 6·42 | .... | 6·65 | |
| 5HgCl | 677·0 | .... | 84·16 | .... | 85·56 | .... | 85·23 | |
| 8HO | 72·0 | .... | 8·95 | .... | 8·02 | .... | 8·12 | |
| CaCl,5HgCl + 8Aq | 804·4 | .... | 100·00 | .... | 100·00 | .... | 100·00 | |

Gay-Lussac & Thénard did not succeed, even with the voltaic battery of the Polytechnic School at Paris, in forming any compound of mercury with an earth-metal.

## Mercury and Magnesium.

A. Magnesium-amalgam.—1. Magnesium combines with mercury only when heated, and forms a solid amalgam, even with large quantities of the latter. (Bussy.)—2. By the galvanic method. (III. 222, 3 and 4.)—3. By covering potassium or sodium-amalgam with solution of sulphate of magnesia. (Klauer, *Ann. Pharm.* 10, 89.)—The amalgam obtained by (2), oxidizes slowly in pure water, quickly in acidulated water. (H. Davy.)

B. Iodide of Mercury and Magnesium.—Aqueous iodide of magnesium, saturated at a high temperature with iodide of mercury, deposits a portion of it on cooling; and the remaining liquid yields greenish

needles, probably composed of MgI,2HgI; these crystals, when digested in water, yield iodide of mercury, and a solution, which probably contains MgI,HgI. (Boullay.)

C. BROMIDE OF MERCURY AND MAGNESIUM.—The solution of bromide of mercury in aqueous bromide of magnesium yields, when evaporated over sulphuric acid, first, broad laminæ, permanent in the air [MgBr, 2HgBr?], and afterwards, very deliquescent crytals [MgBr,HgBr?]. (Bonsdorff.)

D. CHLORIDE OF MERCURY AND MAGNESIUM.—Aqueous hydrochlorate of magnesia, of specific gravity 1·58, dissolves, especially when gently heated, a large quantity of corrosive sublimate, and forms an oily solution, of specific gravity 2·83, which, when cooled, yields a large quantity of needles, and on evaporation, greyish-white, deliquescent crusts. (J. Davy.)—A solution of hydrochlorate of magnesia saturated with corrosive sublimate, yields, on gentle evaporation, first, laminated crystals of the salt *b*, and then, when poured off from the latter and evaporated over sulphuric acid, rhombic crystals of salt *a*.

| | *Anhydrous.* | | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|---|
| MgCl..... | 47·4 | .... | 25·93 | MgCl..... | 47·4 | .... | 20·02 | .... 20·33 |
| HgCl..... | 135·4 | .... | 74·07 | HgCl..... | 135·4 | .... | 57·17 | .... 57·77 |
| | | | | 6HO..... | 54·0 | .... | 22·81 | .... 21·90 |
| MgCl,HgCl | 182·8 | .... | 100·00 | +6Aq. .... | 236·8 | .... | 100·00 | .... 100·00 |

*b. Ter-acid.*—Rhombic laminæ, which, when struck, split into very oblique rhombs, like gypsum; by very slow evaporation, the salt is obtained in large prisms with numerous faces, similar to the crystals of Glauber's salt. The salt is permanent in the air, not undergoing any alteration even at 60° or 70°. When immersed in water, it becomes milky at the first instant, but afterwards dissolves completely, forming a solution which, when left to spontaneous evaporation, yields the same crystals again. (Bonsdorff, *Pogg.* 17, 133.)

| | *Anhydrous.* | | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|---|
| MgCl..... | 47·4 | .... | 10·45 | MgCl..... | 47·4 | .... | 9·51 | .... 9·65 |
| 3HgCl ..... | 406·2 | .... | 89·55 | 3HgCl .... | 406·2 | .... | 81·47 | .... 81·08 |
| | | | | 5HO ..... | 45·0 | .... | 9·02 | .... 9·27 |
| MgCl,3HgCl | 453·6 | .... | 100·00 | +5Aq. .... | 498·6 | .... | 100·00 | .... 100·00 |

## MERCURY AND CERIUM.

CHLORIDE OF MERCURY AND CERIUM.—Cubes permanent in the air. (Bonsdorff.)

## MERCURY AND YTTRIUM.

CHLORIDE OF MERCURY AND YTTRIUM.—Cubes which appear to be deliquescent. (Bonsdorff.)

## MERCURY AND GLUCINUM.

CHLORIDE OF MERCURY AND GLUCINUM.—Right rhombic prisms. (Bonsdorff.)

## Mercury and Aluminum.

Aluminum-amalgam.—Potassium-amalgam introduced into a hole bored in a crystal of alum, immediately acquires a rotatory motion which lasts for half an hour; at the same time, it takes up a considerable quantity of aluminum and becomes more viscid. (Klauer.)

## Mercury and Zirconium.

Zirconium-amalgam.—When potassium-amalgam, connected with the negative pole of a voltaic battery, is placed in contact with zirconia slightly moistened and connected with the positive pole, it acquires the property of depositing, on immersion in water, a white powder, which exhibits the characters of zirconia. (H. Davy.)

## Mercury and Silicium.

A. Silicate of Mercurous Oxide, or Mercurous Silicate.—Quadrosilicate of soda gives a white precipitate with mercurous nitrate.—It does not precipitate a solution of corrosive sublimate; but the mixed solutions yield very small, dark crystals on evaporation, or even without evaporation if they are concentrated. (Walcker.)

B. Mercurous Silicofluoride.—$Hg^2F,SiF^2$.—Formed by digesting mercurous oxide, recently precipitated and still moist, with hydrofluosilicic acid, which gives it a pale yellow colour; part of the acid compound dissolves in the liquid, and separates in small crystals on evaporation. The salt has a faint metallic taste, dissolves sparingly in pure water, more freely in acidulated water; it is precipitated by hydrochloric acid. (Berzelius.)

C. Mercuric Silicofluoride.—$HgF,SiF^2$.—By dissolving mercuric oxide in hydrofluosilicic acid and evaporating.—Small needles, of a very pale yellow colour.—These crystals, when subjected to distillation, yield gaseous fluoride of silicium, whereupon the protofluoride of mercury, more or less decomposed in the manner already mentioned, volatilizes. In contact with water, the crystals are resolved into an *acid solution* and a *basic salt*, which is blackened by ammonia, and afterwards restored to a lighter colour by water. They dissolve completely in acidulated water, forming an acid solution, which, by spontaneous evaporation, can be brought only to a syrupy consistence, and does not yield crystals till evaporated by heat. (Berzelius, *Pogg.* 1, 200.)

## Mercury and Tungsten.

A. Tungstate of Mercurous Oxide.—Mercurous nitrate forms, with tungstate of soda, a yellow precipitate, tasteless at first, but afterwards exhibiting a faint metallic taste; it is insoluble in water, turns deep yellow when dried at a strong heat, and yields greenish-yellow tungstic acid when ignited. (Anthon.)—As this salt is insoluble in water, it serves for the quantitative estimation of tungstic acid united with

alkalis. The alkali, which perhaps is somewhat in excess, is saturated with nitric acid, till the tungstic acid begins to fall down; the solution is then mixed with mercurous nitrate, a little ammonia added for greater security, and the precipitate washed and ignited. (Berzelius.)

| | | | Anthon. |
|---|---|---|---|
| $Hg^2O$ | 208 | 63·41 | 63 |
| $WO^3$ | 120 | 36·59 | 37 |
| $Hg^2O,WO^3$ | 328 | 100·00 | 100 |

B. Tungstate of Mercuric Oxide, or Mercuric Tungstate.—*a. Sesquibasic.*—By precipitating a boiling solution of corrosive sublimate with less than an equivalent quantity of monotungstate of soda. Heavy white powder, having a faint metallic taste. Boiling soda-ley converts it into red oxide of mercury. It is insoluble in water. Tungstate of soda in excess forms, with solution of corrosive sublimate, not a white, but a yellow, red, or black precipitate, or all three together; in the latter case, they may be separated by levigation. The black precipitate, which is produced by a large excess of tungstate of soda at a boiling heat, appears to consist of oxychloride of mercury. (Anthon.)

*b. Sesqui-acid.*—Formed, when a solution of mercuric nitrate, rendered as neutral as possible, is precipitated by monotungstate of soda.—White powder, insoluble in water. Leaves tungstic acid when ignited. (Anthon, *Repert.* 76, 349.)

| | *a.* | | Anthon. |
|---|---|---|---|
| 3HgO | 324 | 57·45 | 56·0 |
| $2WO^3$ | 240 | 42·55 | 43·7 |
| $3HgO,2WO^3$ | 564 | 100·00 | 99·7 |

| | *b.* | | Anthon. |
|---|---|---|---|
| 2HgO | 216 | 37·5 | 38 |
| $3WO^3$ | 360 | 62·5 | 63 |
| $2HgO,3WO^3$ | 576 | 100·0 | 101 |

C. Mercurous Sulphotungstate.—$Hg^2S,WS^3$.—Black precipitate. (Berzelius.)

D. Mercuric Sulphotungstate.—$HgS,WS^3$.—When solutions of corrosive sublimate and sulphotungstate of potassium are mixed in equivalent proportions, orange-yellow flakes are produced, which turn yellowish brown on drying, yield a deep red powder, and acquire lustre under the burnishing steel. The salt, when ignited, yields sulphur, cinnabar, and a residue of bisulphide of tungsten. If the solution of corrosive sublimate is in excess, a precipitate is obtained, which soon turns white; excess of sulphotungstate of potassium produces a black precipitate. If the solution of corrosive sublimate be precipitated by the compound of sulphotungstate of potassium with tungstate of potash (III. 46), the precipitate has the same yellow colour as the pure salt, but takes no polish under the burnisher, and gives off a large quantity of sulphurous acid when ignited. (Berzelius.)

E. Tungstate of Mercuric Oxide and Ammonia.—Bitungstate of ammonia mixed with a solution of mercuric nitrate rendered as neutral as possible, forms a heavy white precipitate. This precipitate, after being dried at 100°, gives off more water and ammonia, at temperatures

between 200° and 500°, and leaves a mixture of mercuric tungstate and free tungstic acid; for the residue renders water milky, an effect produced only by free tungstic acid. The salt is decomposed by acids and alkalis, and does not dissolve in water. (Anthon.)

| | *Approximate Calculation.* | | | Anthon. |
|---|---|---|---|---|
| HgO | 108 | 28·20 | | 28·5 |
| $2WO^3$ | 240 | 62·66 | | 62·4 |
| $NH^5$ | 17 | 4·44 | } | 8·9 |
| 2HO | 18 | 4·70 | } | |
| | 383 | 100·00 | | 99·8 |

## Mercury and Molybdenum.

A. Molybdate of Mercurous Oxide, or Mercurous Molybdate. —Molybdate of potash added to a solution of mercury in nitric acid forms a white precipitate (yellow, according to Berzelius), soluble in 500 or 600 parts of water, and decomposed by nitric acid. (Hatchett.) A solution of corrosive sublimate is not precipitated by molybdic acid. (Scheele.)

B. Mercurous Sulphomolybdate.—$Hg^2S, MoS^3$.—Mercurous nitrate forms with sulphomolybdate of potassium dissolved in water, a black-brown precipitate, which, when ignited, is resolved into cinnabar, which distils over, and a residue of bisulphide of molybdenum. (Berzelius.)

C. Mercuric Sulphomolybdate.—$HgS, MoS^3$.—Formed by precipitating a solution of corrosive sublimate with an alkaline sulphomolybdate. Light brown precipitate, which is not altered by an excess of the potassium-compound, is soon decomposed and turned white by excess of acid, whilst the liquid acquires a blue colour. The precipitate, when dry, yields a dark brown powder, and, when subjected to distillation, gives off, first sulphur, then cinnabar, and leaves bisulphide of molybdenum. (Berzelius, *Pogg.* 7, 277.)

D. Mercurous Persulphomolybdate. — $Hg^2S, MoS^4$. — Red brown precipitate. (Berzelius.)

E. Mercuric Persulphomolybdate.—$HgS, MoS^4$.—Red precipitate. (Berzelius.)

## Mercury and Vanadium.

A. Vanadite of Mercuric Oxide, or Mercuric Vanadite.— Ammonia added to a mixture of corrosive sublimate and a salt of vanadic oxide, throws down a mixture of mercuric vanadite and white precipitate, which, when heated to redness, leaves vanadic oxide, with a small quantity of mercuric oxide; from this precipitate, the vanadic oxide may be precipitated by carbonate of ammonia. This is the most accurate method of precipitating vanadium from its solutions, and determining it quantitatively. (Berzelius, *Lehrb.*)

B. Vanadiate of Mercurous Oxide, or Mercurous Vanadiate.— *a. Mono-acid.*—Mercurous nitrate forms with monovanadiate of ammonia

a milky liquid of a dark yellow colour, which, after a while, deposits a small quantity of solid matter, and is converted into a clear, deep yellow solution.—*b. Bivanadiate.*—Bivanadiate of ammonia added to a solution of mercury, immediately throws down an orange-yellow precipitate. (Berzelius.)

C. VANADIATE OF MERCURIC OXIDE, or MERCURIC VANADIATE.—*a. Monovanadiate.*—A lemon-yellow precipitate is formed by double decomposition; but the liquid remains yellow, inasmuch as the salt is slightly soluble in water. It fuses and crystallizes on cooling; is but imperfectly decomposed by ignition, a large proportion of mercuric oxide still remaining with it; but when it is ignited with carbonate of soda, the whole of the mercury is given off.—*b. Bivanadiate.*—Yellow, soluble in water, and not precipitated from the solution by alcohol. (Berzelius.)

## MERCURY AND CHROMIUM.

A. CHROMATE OF MERCUROUS OXIDE, or MERCUROUS CHROMATE.—*a. Basic.*—Formed by precipitating mercurous nitrate with chromate of potash. (IV. 144.) The presence of nitrous acid prevents the precipitation by converting the chromic acid into chromic oxide. If an excess of nitric acid is present, part of the chromic acid likewise acts upon the mercurous oxide in such a manner as to form mercuric oxide and nitrate of chromic oxide, the liquid acquiring an amethyst colour; on further addition of mercurous nitrate, however, the whole of the chromium is precipitated in the form of mercurous chromate. (Vauquelin, Marx, *Schw.* 66, 107.)

Bright red powder, exhibiting a colour intermediate between brick-red and scarlet. Turns black when exposed to light. At a red heat, it is resolved into oxygen gas, vapour of mercury, and chromic oxide. (Vauquelin, Godon de St. Menin, *A. Gehl.* 5, 598.) Ammonia converts it into a black powder, which, together with the mercurous oxide, contains about half the chromium in the form of chromic oxide. Hydrochloric acid resolves it into calomel and chromic acid. It is slightly soluble in nitric acid. (Hayes.) It dissolves very sparingly in cold water, more freely in boiling water, partly in the form of mercuric salt. (H. Rose, *Pogg.* 53, 124.) It is slightly soluble in aqueous hydrochlorate and nitrate of ammonia. (Brett.)

| | | | | | Godon. | | Gm. |
|---|---|---|---|---|---|---|---|
| 16Hg | 1600 | .... | 80·97 | .... | 80·0 | .... | 79·86 |
| 8O | 64 | .... | 3·24 | } | | | |
| 9O | 72 | .... | 3·64 | } | | .... | 6·51 |
| $3Cr^2O^3$ | 240 | .... | 12·15 | .... | 12·6 | | 12·32 |
| $4Hg^2O,3CrO^3$ .... | 1976 | .... | 100·00 | .... | | | 98·69 |

In both analyses, the salt was decomposed by distillation; in Gmelin's analysis, the oxygen was determined by measure; the loss arose from small quantities of water and nitric acid.

¶ *b. Neutral.*—The precipitate *a*, when boiled with nitric acid, is converted into a crystalline powder, which is the neutral chromate. The same compound is also formed when corrosive sublimate or mercuric nitrate is added to a solution of the compound of chromate of potash with cyanide of mercury, $2(KO,CrO^3) + 3HgCy$, a small quantity of nitric acid being added, just sufficient to dissolve the precipitate, and the solu-

tion heated almost to the boiling point; the salt then separates, on cooling, in the form of a fine red crystalline powder. The whole of the mercury in this salt is precipitated, by hydrochloric acid from its solution in nitric acid. Ammonia and potash form black precipitates with it.

| | | | | | Darby. |
|---|---|---|---|---|---|
| $Hg^2O$ | 208·0 | .... | 80·0 | | |
| $CrO^3$ | 52·0 | .... | 20·0 | .... | 19·1 to 19·5 |
| $Hg^2O,CrO^3$ | 260·0 | .... | 100·0 | | |

(Darby, *Chem. Soc. Qu. J.* I., 24.) ¶

B. Chromate of Mercuric Oxide, or Mercuric Chromate.—Monochromate of potash forms with mercuric nitrate and corrosive sublimate (not with bromide of mercury, according to Caillot), a precipitate having the colour of the basic mercurous salt, and the liquid takes up bichromate of potash. It dissolves in excess of the nitrate and hydrochlorate of mercuric oxide, most easily in the latter, forming a yellow solution. (Gm.)

¶ C. Bichromate of Ammonia with Protochloride of Mercury.—When equivalent quantities of bichromate of ammonia and corrosive sublimate are dissolved in water and the liquid evaporated, deep red crystals are obtained, having the following composition. (Darby.)

| | | | | | Darby. |
|---|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 6·63 | | |
| $2CrO^3$ | 104·0 | .... | 40·56 | .... | 40·4 to 40·8 |
| HgCl | 135·4 | .... | 52·81 | | |
| $NH^3,2CrO^3 + HgCl$ | 256·4 | .... | 100·00 | | |

Messrs. Richmond and Abel, who have lately examined this salt, (*Chem. Soc. Qu. J.* 3, 202), find that it contains, not $NH^3,2CrO^3$ but $NH^4O,2CrO^3$, and that its composition varies according to the strength of the solution from which it crystallizes. About equal weights of bichromate of ammonia ($NH^4O,2CrO^3$) and corrosive sublimate were dissolved together in a rather large quantity of water, and the solution allowed to cool, whereupon a portion of the protochloride of mercury separated out and was removed. The solution was then evaporated down just sufficiently to cause the formation of a few crystals on cooling. These crystals were beautiful, large, six-sided prisms, of a splendid red colour; they were dried on blotting paper, and afterwards in vacuo over sulphuric acid. On further evaporation, the liquid yielded a second crop of crystals, having the same appearance as the first; and the mother-liquor, when still further evaporated, yielded more crystals, much resembling the former, but rather more inclined to the needle shape. The product of the first and second crystallizations gave, on analysis, results agreeing with the formula $NH^4O,2CrO^3 + HgCl + Aq.$; that of the third, $3(NH^4O,2CrO^3)$, HgCl.

| | *1st and 2nd Crystallizations.* | | | | Richmond & Abel. |
|---|---|---|---|---|---|
| $2CrO^3$ | 104·0 | .... | 37·96 | .... | 37·9 to 38·19 |
| Hg | 100·0 | .... | 36·39 | .... | 96·2 ,, 36·49 |
| Cl | 35·5 | .... | 12·92 | | |
| N | 14·0 | .... | 5·09 | | |
| 5H | 5·0 | .... | 1·82 | .... | 1·83 ,, 1·87 |
| 2O (as water) | 16·0 | .... | 5·82 | | |
| $NH^4O,2CrO^3 + HgCl + Aq.$ | 274·5 | ..... | 100·00 | | |

| | *3rd Crystallization.* | | | | Richmond & Abel. |
|---|---|---|---|---|---|
| $6CrO^3$ | 312·0 | .... | 59·44 | .... | 59·43 to 59·52 |
| Hg | 100·0 | .... | 18·99 | .... | 18·90 ,, 18·91 |
| $3NH^3$ | 51·0 | .... | 9·69 | | |
| 3HO | 27·0 | .... | 5·13 | | |
| Cl | 35·5 | .... | 6·75 | | |
| $3(NH^4O,2CrO^3) + HgCl$ | 525·5 | .... | 100·00 | | |

Mr. Darby's salt appears to have contained an excess of corrosive sublimate.

D. Monochromate of Potash with Protochloride of Mercury. —1. When a solution of monochromate of potash is mixed with corrosive sublimate, a brick-red precipitate is formed, consisting of mercuric chromate, B; and on evaporating the solution filtered from that precipitate, small crystals are formed, of a pale red colour, which readily dissolve in water, yielding a yellow solution.—2. The same salt is also formed on mixing equivalent quantities of chromate of potash and chloride of mercury, or 2 equivalents of the former to 1 equivalent of the latter, and adding just sufficient hydrochloric acid to dissolve the precipitate formed on mixing the solutions. (Darby.)

| | | | | | Darby. | | |
|---|---|---|---|---|---|---|---|
| KO | 47·2 | .... | 12·76 | .... | 13·3 | .... | 12·1 |
| $CrO^3$ | 52·0 | .... | 14·05 | .... | 13·3 | .... | 13·4 |
| 2Hg | 200·0 | .... | 54·05 | .... | | .... | 51·2 |
| 2Cl | 70·8 | .... | 19·14 | .... | 21·3 | .... | 21·1 |
| $KO,CrO^3 + 2HgCl$ | 370·0 | .... | 100·00 | .... | | .... | 97·8 |

E. Bichromate of Potash with Protochloride of Mercury.— On evaporating a solution containing equivalent quantities of bichromate of potash and corrosive sublimate, this double salt is obtained in beautiful red-pointed crystals, which are anhydrous. (Darby.)

| | | | | | Darby. |
|---|---|---|---|---|---|
| KO | 47·2 | .... | 16·48 | | |
| $2CrO^3$ | 104·0 | .... | 36·28 | .... | 34·55 |
| Hg | 100·0 | .... | 34·89 | .... | 36·60 |
| Cl | 35·4 | .... | 12·35 | .... | 14·80 |
| $KO,2CrO^3 + HgCl$ | 286·6 | .... | 100·00 | | |

The excess of chlorine is accounted for by a portion of the chromic acid being precipitated, and not entirely re-dissolved even by hot nitric acid. (Darby.) ¶

## Mercury and Manganese.

A. Manganese-amalgam.—Sodium-amalgam, immersed in a strong solution of chloride of manganese. evolves hydrogen gas, takes up a considerable quantity of manganese, and is converted into a viscid mass, having an uneven, blackish surface. When freed from the watery liquid by pressure between bibulous paper, and then heated in the air, it assumes a succession of tints like steel; gives off mercury, and is converted into a stiff paste; and finally leaves a residue of brown manganoso-manganic oxide. The amalgam, when immersed in water, liberates bubbles of hydrogen gas,—more rapidly in acidulated water; if it be then touched

with a platinum wire, the evolution of gas becomes violent. (Böttger, *J. pr. Chem.* 12, 350.) In a strong solution of manganous sulphate, sodium-amalgam causes an evolution of hydrogen gas, and separates manganous oxide. (Böttger, *J. pr. Chem.* 3. 283.)

Permanganate of potash gives no precipitate with solution of corrosive sublimate. (Frombery.)

B. Bromide of Mercury and Manganese.—Light red prisms, which soon become moist, even in tolerably dry air. (Bonsdorff.)

C. Chloride of Mercury and Manganese.—Aqueous chloride of manganese, saturated with corrosive sublimate, and evaporated over sulphuric acid in a chamber containing air, deposits corrosive sublimate at first, and afterwards yields large, transparent, light red, right rhombic prisms. *Fig.* 65, without the *t*-face, $i : i' = 86\frac{1}{2}°$ to 70°, $u' : u$ about = 114°; also prisms with 6, 8, and 10 sides [perhaps *Fig.* 74?]. The crystals effloresce in the evaporating chamber, but are permanent in tolerably dry air, and deliquesce rapidly in moist air. (Bonsdorff.)

| | *Anhydrous.* | | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|---|
| MnCl..... | 63·4 | .... | 31·89 | MnCl..... | 63·4 | .... | 27·00 | .... 26·15 |
| HgCl..... | 135·4 | .... | 68·11 | HgCl..... | 135·4 | .... | 57·67 | .... 57·60 |
| | | | | 4HO ..... | 36·0 | .... | 15·33 | .... 16·25 |
| MnCl,HgCl.. | 198·8 | .... | 100·00 | +4Aq. .... | 234·8 | .... | 100·00 | .... 100·00 |

## Mercury and Arsenic.

A. Amalgam of Arsenic.—When pounded arsenic is heated over a fire with mercury, and the mixture stirred, a grey compound is obtained, containing 5 pts. mercury and 1 pt. arsenic. (Beryman.)—Dranty (*J. Chim. méd.* 12, 650) sublimes in a tube an intimate mixture of mercuric oxide, arsenious acid, and charcoal. According to Lassaigne, however (*ibid.*), this process does not yield the amalgam, but a mixture of mercury, metallic arsenic, and arsenious acid.—Sodium-amalgam, placed in contact with moistened arsenious acid, becomes heated immediately, and separates arsenic in the form of a black-brown film, but does not take any of it up. (Böttger.)

B. Arsenite of Mercurous Oxide, or Mercurous Arsenite.—Aqueous arsenious acid and arsenite of potash yield, with mercurous nitrate, a white precipitate, soluble in nitric acid.—If the arsenite of potash has been obtained by decomposing arsenite of baryta with sulphate of potash, it forms, with mercurous nitrate, a permanent white precipitate; but aqueous potash, saturated at a boiling heat with arsenious acid, and freed from an excess of that substance by cooling, yields a white precipitate, which soon turns grey, and blackens on the application of heat. (Simon, *Pogg.* 40, 442.)—Can the arsenite of potash prepared by the latter process also contain carbonate?—The same salt is obtained by digesting mercury with arsenious acid. (Berzelius.)

C. Arsenite of Mercuric Oxide, or Mercuric Arsenite.—Arsenious acid, added to mercuric nitrate, throws down a white powder which dissolves in arsenite of potash, forming a brownish solution, and likewise in nitric acid.

D. Arseniate of Mercurous Oxide, or Mercurous Arseniate.—*a. Bibasic.*—Mercurous nitrate, dropped into a concentrated solution of arsenic-acid, forms a white precipitate, which at first re-dissolves in the excess of arsenic acid, but becomes permanent on the addition of a larger quantity of the mercurial solution. It remains white during washing, but becomes red when dry.—2. When arsenic acid or arseniate of soda is added to the mercurous solution, a white compound of mercurous arseniate with mercurous nitrate, is first precipitated; but it soon turns yellow, then red, and ultimately assumes the purple-red tint of pure mercurous arseniate, the change being greatly accelerated by heat.—When the salt prepared according to (1) or (2), is dissolved in warm nitric acid, and the acid gradually neutralized with ammonia, a black precipitate is produced, which turns red when continuously heated. (Simon.)

Sometimes brown-red, sometimes purple-red; composed of fine needles. When dried at 100°, and afterwards more strongly heated, it evolves a small quantity of water of crystallization, afterwards gives off mercury, and leaves yellow mercuric arseniate, which, at a higher temperature, is resolved into mercury, arsenious acid, and oxygen gas. With cold concentrated hydrochloric acid, it yields a solution of arsenious acid and a residue of calomel, which is resolved, by boiling, into mercury and soluble corrosive sublimate. The salt is converted into mercuric arseniate by boiling with nitric acid, but dissolves unchanged in that acid when cold, and is precipitated from the solution by ammonia. Dissolves very sparingly in aqueous nitrate of ammonia, from which it separates on evaporation, with a fine red colour and crystalline structure. Quite insoluble in water, acetic acid, and ammonia. (Simon, *Pogg.* 41, 424.)

| | *Anhydrous.* | | Simon. | | *Crystallized.* | | Simon. |
|---|---|---|---|---|---|---|---|
| $2Hg^2O$ | 416 | 78·34 | 80·1 | $2Hg^2O$ | 416 | 75·77 | 77·25 |
| $AsO^5$ | 115 | 21·66 | 19·9 | $AsO^5$ | 115 | 20·95 | 19·20 |
| | | | | 2HO | 18 | 3·28 | |
| $2Hg^2O,AsO^5$ | 531 | 100·00 | 100.0 | +2Aq. | 549 | 100·00 | |

*b. Monobasic.*—Formed by boiling mercuric oxide, or salt *a*, to dryness, with aqueous arsenic acid, triturating the white mass when cold with water, washing the powder, and drying it in the water-bath, by which the whole of the water is expelled.—White, not crystalline.—At a red heat, it gives off mercury, and is converted into mercuric arseniate, which then undergoes further decomposition. By careful addition of potash, it is converted into salt *a*. With hydrochloric acid, and with boiling nitric acid, it behaves like the salt *a*. Dissolves less abundantly than the latter in cold nitric acid, and on the application of heat and the gradual addition of ammonia, it is precipitated from the solution in the form of the salt *a*. Insoluble in water, acetic acid, and alcohol. (Simon.)

| | | | Simon. |
|---|---|---|---|
| $Hg^2O$ | 208 | 64·4 | 62·66 |
| $AsO^5$ | 115 | 35·6 | 37·34 |
| $Hg^2O,AsO^5$ | 323 | 100·0 | 100·00 |

E. Arseniate of Mercuric Oxide, or Mercuric Arseniate.—Arsenic acid forms with mercuric nitrate, and arseniate of soda forms with solution of corrosive sublimate, a yellow precipitate, soluble in arsenic acid and in nitric acid. Yellow mercuric arseniate is also obtained by heating mercury with dry arsenic acid, the action being attended with evolution of arsenious acid. (Bergman.)

F. Mercurous Sulpharsenite.—$2Hg^2S,AsS^3$.—Formed by precipitating mercurous nitrate with a saturated solution of orpiment in aqueous sulphide of sodium. Black precipitate. When heated, it decrepitates violently, gives off mercury, and then sublimes in the form of G, *a*. (Berzelius.)

G. Mercuric Sulpharsenite.—*a. Bibasic.*—$2HgS,AsS^3$.—Formed by the sublimation of F. Dark coloured, nearly black; shining, opaque; forms a dark red powder. (Berzelius.)

*b. Monobasic.*—$HgS,AsS^3$.—Formed by precipitating corrosive sublimate. The solution of corrosive sublimate must not be in excess, otherwise it will decompose the precipitate, and turn it white. Orange-yellow flakes, which become dark brown and deep yellow after drying. When heated, it fuses and sublimes without decomposition, forming a translucent yellowish mass, having the metallic lustre and a grey colour on the oblique fracture, and likewise yielding a yellow powder. (Berzelius, *Pogg.* 7, 149.)

H. Mercurous Sulpharseniate.—$2Hg^2S,AsS^5$.—Formed by precipitating a mercurous salt. The black precipitate, when heated, gives off mercury with violent decrepitation, and then sublimes in the form of the salt I.

I. Mercuric Sulpharseniate.—$2HgS,AsS^5$.—1. By sublimation of H. —2. Both bibasic and terbasic sulpharseniate of sodium form, with mercuric salts, a deep yellow precipitate, which sublimes without decomposition. The sublimate is black, shining, and yields a dingy red powder. (Berzelius, *Pogg.* 7, 29.)

K. Chlorarsenide of Mercury.—*a.* $Hg^3As,3HgCl$, or $As,3Hg^2Cl$. —The precipitate which arseniuretted hydrogen gas produces in a solution of corrosive sublimate. It must be washed with cold water, and quickly dried in vacuo. Brownish yellow. When heated in a glass tube, it gives off arsenic and calomel, without evolution of gas, and forms an orange-white sublimate, probably consisting of the undecomposed compound. If kept under a large quantity of water, after being washed, it turns black, and is finally resolved into globules of mercury, while the water takes up hydrochloric acid and arsenious acid:

$$Hg^6,As,Cl^3 + 3HO = 6Hg + AsO^3 + 3HCl.$$

It is therefore necessary, in passing the arsenuiretted hydrogen through the solution of corrosive sublimate, to leave a portion of the latter unprecipitated; by this precaution, the precipitate is preserved from decomposition. This compound is converted into calomel by immersion in slightly-warmed nitric acid. (H. Rose, *Pogg.* 51, 423.)

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| 6Hg | 600·0 | .... | 76·8 | .... | 76·80 |
| As | 75·0 | .... | 9·6 | | |
| 3Cl | 106·2 | .... | 13·6 | .... | 13·13 |
| $Hg^3As,3HgCl$ | 781·2 | .... | 100·0 | | |

*b.* $Hg^2As,2HgCl$, or $As,2Hg^2Cl$.—Berzelius (*Schw.* 21, 339), by heating arsenic with calomel, obtained a small quantity of terchloride of arsenic, and a brown-red, partly-transparent sublimate, which yielded a

yellow powder, and contained mercury, arsenic, and chlorine.—This compound is formed by heating an intimate mixture of 1 pt. arsenic and 3 pts. calomel in a flask immersed in a sand-bath, till the greater part is sublimed. At the bottom of the flask there remains a hard, reddish yellow mass, containing globules of mercury; the sublimate consists of three substances, viz., a yellow or reddish yellow, hard, compact mass, of variable composition, on which there rest small, opaque, brown, dendritic crystals of the following compound *c*, and larger hyacinth-red crystals of the compound *b*, now under consideration.

The reddish yellow powder of this compound blackens very slowly when exposed to sun-light. When heated, it partly volatilizes undecomposed, and is partly resolved into mercury, arsenic, and terchloride of arsenic:

$$3(Hg^4,As,Cl^2) = 12Hg + As + 2AsCl^3.$$

Under water, especially if boiling, it is completely converted into mercury, arsenic, and a solution of arsenious and hydrochloric acid.

$$3(Hg^4,As,Cl^2) + 6HO = 12Hg + As + 2AsO^3 + 6HCl.$$

Corrosive sublimate heated with arsenic likewise yields a brown-red sublimate, but a large quantity of terchloride of arsenic is likewise formed. (Capitaine.)

| | | | | Capitaine. |
|---|---|---|---|---|
| 4Hg | 400·0 | 73·29 | .... | 68—70—71—73—75 |
| As | 75·0 | 13·74 | | |
| 2Cl | 70·8 | 12·97 | .... | 12—14 |
| $Hg^2As,2HgCl$ | 545·8 | 100·00 | | |

From the various results obtained in the analysis of different samples of this compound, Capitaine concludes that it was mixed with variable quantities of the compound *c*.

*c*. $HgAs,HgCl$, or $As,Hg^2Cl$.—Obtained as a sublimate, together with *b*, in brown, dendritic crystals. The yellow powder of this compound, when exposed to sunlight, even in a dry space exhausted of air, becomes greenish in a few seconds, afterwards darker, and finally black. When heated, it behaves like *b*, being but partially decomposed into mercury, arsenic, and terchloride of arsenic:

$$3(Hg^2,AsCl) = 6Hg + 2As + AsCl^3.$$

It is also decomposed like *b* by immersion in water.

$$3(Hg^2,AsCl) + 3HO = 6Hg + 2As + AsO^3 + 3HCl.$$

(Capitaine, *J. Pharm.* 25, 559; also *J. pr. Chem.* 18, 422.)

| | | | | Capitaine. |
|---|---|---|---|---|
| 2Hg | 200·0 | 64·43 | .... | 64·11 to 65·18 |
| As | 75·0 | 24·16 | .... | 23·50 „ 22·93 |
| Cl | 35·4 | 11·41 | .... | 11·76 „ 11·89 |
| $HgAs,HgCl$ | 310·4 | 100·00 | .... | 99·37 „ 100·00 |

L. Nitro-arseniate of Mercurous Oxide.—1. When a solution of bibasic mercurous arseniate in tolerably strong nitric acid is covered with an equal volume of water, aqueous ammonia poured upon that, and the whole left to stand quietly for some time, the double salt is deposited in white warty masses and needles. If the liquids are mixed too suddenly, the product becomes mixed with a large quantity of grey

powder, and likewise with bibasic mercurous arseniate.—2. On gradually adding to a warm solution of bibasic mercurous arseniate in nitric acid—the liquid being agitated all the while—such a quantity of ammonia that the bibasic mercurous arseniate shall be just on the point of falling down, and then leaving the solution to cool, this compound is obtained in warty masses, but not in needles.—3. The compound is also obtained in the form of a white powder, on adding a very small quantity of arsenic acid to a solution of mercurous nitrate. If too much arsenic be used, the precipitate turns yellow or orange. Yellowish white, warty or needle-shaped. Gives off nitrous acid when heated either alone or with oil of vitriol. From its solution in nitric acid, ammonia added in proper proportion throws down bibasic mercurous arseniate. (Simon, *Pogg.* 41, 424.)

| | *Approximate Calculation.* | | | | Simon. |
|---|---|---|---|---|---|
| $3Hg^2O$ | 624 | .... | 78·69 | .... | 80·24 |
| $AsO^5$ | 115 | .... | 14·50 | .... | 13·34 |
| $NO^5$ | 54 | .... | 6·81 | .... | |
| $2Hg^2O,AsO^5 + Hg^2O,NO^5$ | 793 | .... | 100·00 | | |

## Mercury and Antimony.

A. Antimonial Amalgam.—Mercury does not act upon antimony at ordinary temperatures; combination takes place, however, on pouring 3 parts of heated mercury on 1 part of melted antimony, and triturating the two together for a few minutes. The amalgam is soft, and when triturated for some time in the air, or when agitated with water, gives up its antimony in the form of a black powder. (Wallerius, *Physische Chemie*, 2, 1, 84.) The amalgam may also be formed by triturating 2 parts of antimony in a mortar with a small quantity of hydrochloric acid, and gradually dropping in 1 part of mercury, continuing the friction all the while. (Rudolfi, *ibid.* 85.) When sodium-amalgam is immersed in a saturated solution of tartar-emetic, hydrogen gas [antimoniuretted?] is evolved, having a peculiar odour, and burning with a dazzling white flame, and the antimony is separated in blackish grey, metallic scales, without uniting with the mercury. (Böttger.)

B. Antimoniate of Mercurous Oxide, or Mercurous Antimoniate.—Antimoniate of potash forms, with mercurous nitrate, an orange-yellow precipitate, insoluble in water. Hence mercurous nitrate may be used for the determination of antimonic acid when combined with alkalis, in the same manner as for tungstic acid (p. 111). (Berzelius.)

C. Antimoniate of Mercuric Oxide, or Mercuric Antimoniate.—1. When 1 part of antimony is heated with 8 parts of mercuric oxide, the mass glows; metallic mercury distils over; and this salt is produced in the form of a dark olive-green powder, which sustains a moderate red heat without alteration, but, when more strongly heated, is decomposed, yielding oxygen gas and vapour of mercury, together with a residue of antimony, and afterwards of antimonious acid. This compound is scarcely attacked by alkalis, and by the greater number of acids, even sulphuric acid acting on it but slowly. The small quantity which dissolves in boiling hydrochloric acid is thrown down in the form of a light green precipitate by ammonia.—2. Aqueous antimoniate of potash forms an orange-yellow precipitate with mercuric salts.

D. Mercurous Sulphantimoniate.—$3Hg^2S,SbS^5$.—Schlippe's salt added in any proportion to mercurous salts forms a black precipitate. (Rammelsberg.)

E. Mercuric Sulphantimoniate.—$3HgS,SbS^5$.—Formed by gradually adding a solution of corrosive sublimate to a solution of Schlippe's salt, so that the latter remains in excess. Dark orange-coloured precipitate, becoming brown when dried. (Rammelsberg, *Pogg.* 52, 229.)

When a solution of Schlippe's salt is precipitated with a large excess of solution of corrosive sublimate, or when the precipitate E is heated with that solution, a white substance is formed containing ($3HgS, SbS^5$) + 3HgCl + 3HgO.—This substance, when heated in a retort, assumes a dark colour, gives off sulphurous acid, then mercury and terchloride of antimony, and leaves black sulphide of mercury, which ultimately sublimes.

$$2[(3HgS,SbS^5) + 3HgCl + 3HgO] = 3SO^2 + 2SbCl^3 + 5Hg + 13HgS.$$

Caustic potash immediately blackens the white compound by converting it into pure sulphide of mercury, and taking up antimonic acid (which may be precipitated by nitric acid) together with chlorine. [Is not the sulphide of mercury mixed with red oxide? for:

$$(3HgS,SbS^5) + 3HgCl + 3HgO + 4KO = 8HgS + HgO + KO,SbO^5 + 3KCl.]$$

Simple acids act but slightly on the white compound; but aqua-regia dissolves it easily. (Rammelsberg.)

| | | | | | Rammelsberg. |
|---|---|---|---|---|---|
| 9Hg..... | 900·0 | .... | 69·92 | .... | 70·22 |
| Sb ..... | 129·0 | .... | 10·02 | .... | 9·60 |
| 8S ..... | 128·0 | .... | 9·95 | .... | 9·68 |
| 3Cl ..... | 106·2 | .... | 8·25 | .... | 8·99 |
| 3O ..... | 24·0 | .... | 1·86 | .... | 1·51 |
| | 1287·2 | .... | 100·00 | .... | 100·00 |

## Mercury and Tellurium.

A. Tellurium-amalgam.—Tin-white and granular. (Klaproth, Berzelius.)

B. Tellurite of Mercurous Oxide, or Mercurous Tellurite.—Deep yellow precipitate, which becomes brown after a while, and when exposed to the air, is converted into mercuric tellurite. (Berzelius.)

C. Tellurite of Mercuric Oxide, or Mercuric Tellurite.—This salt, when formed by double decomposition, forms with the liquid a white milk, from which it does not separate. (Berzelius.)

D. Tellurate of Mercurous Oxide, or Mercurous Tellurate.—Finely pounded crystallized mercurous nitrate, immersed in an aqueous solution of monotellurate of potash, forms a dark yellowish brown precipitate. When a solution of mercurous nitrate is precipitated by tellurate of potash, the precipitate is likewise yellowish brown, but is soon turned pale yellow by the action of the free acid in the mercurous solution, being probably converted into *bitellurate* of mercurous oxide.

E. Tellurate of Mercuric Oxide, or Mercuric Tellurate.—Bulky white flakes. (Berzelius.)

F. Mercurous Sulphotellurite.—$3Hg^2S,TeS^2$.—The dark brown precipitate, when heated, gives off mercury with a hissing noise, and is converted into the following compound.

G. Mercuric Sulphotellurite.—$3HgS,TeS^2$.—Yellowish brown. When strongly heated, it gives off sulphur, and then sublimes in the form of a dark grey mixture of sulphur and telluride of mercury, which yields a blackish grey powder. (Berzelius.)

## Mercury and Bismuth.

Bismuth-amalgam.—Mercury quickens bismuth even at ordinary temperatures; but the amalgam is more speedily formed by pouring 2 parts of hot mercury into 1 part of melted bismuth. The amalgam, which is soft at first, gradually becomes crystallo-granular. Sodium-amalgam in contact with moist mononitrate of bismuth-oxide, or immersed in a solution of bismuth-nitrate, forms a compact amalgam with evolution of hydrogen, and separation of black pulverulent bismuth. (Böttger.)—A small quantity of bismuth takes away but little of the fluidity of mercury, and is therefore used for adulterating that metal; according to Lucas, however (*N. Tr.* 10. 1, 195), mercury adulterated with only $\frac{1}{8000}$ part of bismuth forms a black powder when agitated in the air. 1 part of bismuth dissolved even in 1,200,000 parts of mercury may be detected by the addition of potassium-amalgam and water, the bismuth being then raised by the galvanic action in the form of a black powder, and attaching itself to the sides of the vessel. (Serullas, *Ann. Chim. Phys.* 34, 192.)

## Mercury and Zinc.

Zinc-amalgam.—When zinc-filings are triturated with mercury, at ordinary temperatures, combination takes place slowly; at a higher temperature, still somewhat under the boiling point of mercury, the metals combine easily, and still more readily when mercury is mixed with melted zinc. A bar of zinc, immersed to half its length in mercury for ten days, becomes pointed at bottom, and covered, especially on the upper part of the immersed end, with six-sided tables of the amalgam. (Daniell.)—When zinc is placed in contact with mercury and a dilute acid, a galvanic action is set up (I, 348), and the zinc becomes covered with mercury, which then penetrates into the interior, and converts the whole of the metal into an amalgam. As soon as the zinc is completely covered with mercury, the evolution of hydrogen ceases; but it begins again on bringing the amalgam in contact with iron, copper, or platinum, to which metals the mercury is then transferred. (Döbereiner, *Schw.* 17, 238.)—Sodium-amalgam immersed in a concentrated solution of sulphate of zinc, forms a viscid amalgam of zinc. (Böttger.)

The amalgam is usually prepared by cooling melted zinc to as low a temperature as it will bear without solidifying, and then pouring in the mercury in a fine stream, keeping the liquid constantly stirred. If

this precaution be neglected, part of the mercury is converted into vapour, sometimes throwing the melted metal about.

8 pts. zinc to 1 pt. mercury: very brittle.

1 pt. zinc and 4 or 5 pts. mercury form the amalgam for Higgins and Adams's electrical machine; it is brittle and pulverulent.

1 pt. zinc to 6 pts. mercury: tin-white, granular, brittle; fuses at the boiling point of olive-oil, but does not give off mercury till raised to a higher temperature. At a dull red heat, it decrepitates strongly; at a stronger red heat, it burns with great brilliancy. It is permanent in dry air. Cold dilute nitric acid decomposes it readily, and leaves the mercury unaltered till all the zinc is dissolved. Dilute sulphuric and hydrochloric acid act on it but slowly. Ammonia and sal-ammoniac also dissolve out the zinc very slowly, and form water. Zinc-amalgam immersed in the solution of a neutral salt of chromium, uranium, manganese, or iron, merely throws down the oxide; but from neutral solutions of cobalt, nickel, and copper, it precipitates the metal, which then combines with the mercury. (Damour, *Ann. Mines.* 3 *Ser.* 15, 41; also *J. pr. Chem.* 17, 345.)

From an amalgam richer in mercury, six-sided laminæ containing 2 pts. zinc and 5 mercury, separate out on cooling. The portion which remains liquid is a solution of zinc in excess of mercury. 1 pt. of zinc dissolved in 8000 pts. of mercury may be detected by the black powder which forms on the surface when the mercury is agitated in the air. (Lucas.)

Zinc-amalgam immersed in caustic potash liberates pure hydrogen gas. (Bischof, *Kastn. Arch.* 1, 193.)—When zinc-amalgam is immersed in aqueous protochloride of iron, and a crystal of a nitrate placed upon it, a black spot is gradually formed on the amalgam, consisting of reduced iron, which is immediately taken up by the mercury. The presence of a nitrate is essential to the production of this effect; chlorates and other salts do not act in the same manner. (Runge, *Pogg.* 9, 479.)

¶ Joule (*Chem. Gaz.* 1850, 339), obtains an amalgam having the composition $Zn^2Hg$ by dissolving zinc in mercury, and forcing out the excess of mercury by very strong pressure. ¶

B. Selenide of Mercury and Zinc.—A grey mineral from Culebras contains about: 24 pts. zinc,—19 mercury,—49 selenium,—1·5 sulphur,—and 6 lime (loss 0·5.) Del Rio (*Schw.* 54, 226.)

C. Iodide of Mercury and Zinc.—Aqueous iodide of zinc saturated with mercuric iodide, yields, when evaporated under a bell-jar over sulphuric acid, first octohedrons and cubes of iodide of mercury, then the double iodide, in yellow, very deliquescent prisms, some of which are rhombic, and others hexagonal with pyramidal summits. (Bonsdorff.)—158 pts. (1 At.) of iodide of zinc dissolved in water, take up, when the liquid is heated, only 431 pts. (not quite 2 At.) of mercuric iodide; the solution deposits part of the mercuric iodide on cooling, and a further quantity on the addition of water. (Boullay.)

D. Bromide of Mercury and Zinc.—Prisms and tables, which are permanent in dry air, but deliquesce in a moist atmosphere. (Bonsdorff.)

E. Chloride of Mercury and Zinc.—The solution of corrosive sublimate in aqueous chloride of zinc deposits on evaporation, beautiful

crystals of corrosive sublimate, after which, very deliquescent needles and tables slowly separate out. (Bonsdorff.)

## Mercury and Cadmium.

A. Cadmium-amalgam.—Combination takes place easily, even at ordinary temperatures. The amalgam is silver-white, crystallo-granular, crystallizes in octohedrons; it is hard and brittle, specifically heavier than mercury, and melts at 75°. When the mercury is completely saturated with cadmium, the alloy contains 78·26 pts. (2 At.) of mercury to 21·74 pts. (1 At.) of cadmium. (Stromeyer.) Sodium-amalgam immersed in a concentrated solution of sulphate of cadmium, is converted into cadmium-amalgam. (Böttger.)

B. Iodide of Mercury and Cadmium.—When cadmium-filings are triturated with moistened protiodide of mercury, the product washed out with water, and the filtrate evaporated, the double iodide separates in small, yellowish-white, very soluble laminæ. (Berthemot, *J. Pharm.* 14, 613.)

## Mercury and Tin.

A. Tin-amalgam.—The two metals unite quickly even at ordinary temperatures, still more quickly on pouring mercury into melted tin. A piece of tin, the lower end of which is immersed for four weeks in mercury, is penetrated through and through by the mercury, and exhibits cracks; its lower end becomes attenuated by solution of the metal, and the immersed part is found to be covered with six-sided tables, some of which float about in the mercury. If a square bar of tin, whether cast in a square form, or hammered or filed square from a round bar, be kept for a few days under mercury, it splits in directions proceeding from the lateral edge to the opposite diagonals, thereby dividing itself into four triangular prisms, easily separated by a knife; at the same time, a four-sided pyramid is formed at each end of the square bar. If the piece of tin has any other form, cracks are produced in other directions. (Daniell, *J. of Roy. Inst.* 1, 1; also *Pogg.* 20, 260.) Sodium-amalgam immersed in a concentrated solution of protochloride of tin, yields a viscid amalgam of tin. (Böttger.)

Tin-amalgam has a tin-white colour, and if the mercury be not in too great excess, is brittle, granular, and according to Daubenton, crystallizes in cubes.

$Sn^2Hg$ and SnHg do not fuse till heated above 100°. (Regnault.)

$Sn^3Hg$ has at 26° a specific gravity of 8·8218;—$Sn^2Hg$: 9·3185;—SnHg: 10·3447;—$SnHg^2$: 11·3816.—1 volume of tin with 1 volume of mercury forms an alloy whose specific gravity at 17° is 10·4729;—1 vol. tin with 2 vol. mercury: 11·4646;—and 1 vol. tin with 3 vol. mercury: 12·0257. In most cases, therefore, condensation takes place; in the single instance of 1 vol. tin to 2 vol. mercury, however this condensation is scarcely perceptible. (Kupffer, *Ann. Chim. Phys.* 40, 293.)

The compound obtained by fusing 4 pts. of tin with 1 pt. of mercury, yields, if pulverized after cooling, a kind of mosaic silver, which, when rubbed on the polishing-stone, acquires the metallic lustre.—The *silvering* of mirrors is likewise an amalgam of tin.

When oil of vitriol is heated with tin-amalgam, and the action interrupted at the proper time, the whole of the mercury is found to be attacked, while the whole of the tin remains in the metallic state. (Brault & Poggiale, *J. Pharm.* 21, 140.) [Probably a misprint in the memoir; it is the tin which is chiefly attacked. *Gm.*]

When the mercury is in very great excess, a liquid is obtained resembling mercury, and to be regarded as a solution of the amalgam in excess of mercury. With a smaller excess of mercury, a soft granular mixture is obtained, consisting of the solid amalgam and its solution in mercury. A solution of 1 pt. tin in 6000 mercury becomes covered with a black scum on agitation in the air. (Lucas.) Potassium-amalgam together with water, separates tin from the liquid amalgam, in the same manner as it separates bismuth from the bismuth-amalgam (p. 122), but more slowly and less distinctly. (Serullas.)

B. Stannate of Mercurous Oxide, or Mercurous Stannate.—Stannate of potash yields with mercurous nitrate a yellow precipitate, which soon turns green, and finally becomes dark-green; it is composed of $Hg^2O,SnO^2 + 5Aq$. (Moberg.)

C. Stannate of Mercuric Oxide, or Mercuric Stannate.—Formed by precipitating mercuric nitrate.—White, but changes to dark-green; composed of $HgO,SnO^2 + 6Aq$. (Moberg, *J. pr. Chem.* 28, 231.)

D. Chloride of Mercury and Tin.—1. Formed by fusing 3 pts. of tin with 1 pt. of mercury; pulverizing the amalgam after cooling, and mixing it with 24 pts. of calomel; and heating the mixture in a glass retort, whose bulk is four times as great as that of the mixture (on account of the frothing), to about 250°, at which temperature the action takes place, accompanied by a disturbance which lasts but for a short time. When the action is over, the retort is left to cool—then broken—the grey spongy mass separated from the mercury which collects below it—afterwards pounded, introduced into a flat-bottomed flask provided with a stopper—and heated in a bath of fusible metal, not above the boiling point of mercury, as long as white fumes continue to go off. Bichloride of tin then escapes, and chloride of mercury and tin sublimes, while protochloride of tin and metallic mercury below it remain in the flask. To obtain the sublimed substance, the flask must be broken without shaking it.—2. The pulverized amalgam, of 3 pts. tin and 1 pt. mercury is heated as above with 3 parts of corrosive sublimate, till, at about 220°, the mixture froths up briskly, giving off fumes of bichloride of tin, and a greyish white powder (consisting of calomel and a small quantity of protochloride of tin) sublimes. The brown mixture of calomel and protochloride of tin is then heated by itself in a retort to 360°, whereupon bichloride of tin volatilizes (because the protochloride takes chlorine from the calomel), and the white compound, mixed with globules of mercury, sublimes, while mercury remains in the retort, together with protochloride of tin, still containing a small quantity of calomel. From this it appears that what the older chemists regarded as pure *Butyrum Stanni*, contains protochloride of tin and likewise calomel in variable proportions.

The compound forms small, dendritic crystals. On the application of heat, part of it volatilizes undecomposed, while the rest is resolved into mercury, protochloride of tin, and bichloride of tin. When water is

poured upon this substance, it turns grey and then black, because the protochloride of tin separates mercury from the calomel; but, even after boiling for a short time, a small portion of calomel remains undecomposed, and the filtrate still contains a small quantity of protochloride of tin, together with bichloride. (Capitaine, *J. Pharm.* 25, 549; also *J. pr. Chem.* 18, 422.)

| | | | | | Capitaine. |
|---|---|---|---|---|---|
| Sn..... | 59·0 | .... | 17·88 | .... | 17·68 |
| 2Hg ..... | 200·0 | .... | 60·65 | .... | 61·31 |
| 2Cl ..... | 70·8 | .... | 21·47 | .... | 21·09 |
| $SnCl,Hg^2Cl$.... | 329·8 | .... | 100·00 | .... | 100·08 |

E. Amalgam of Tin and Bismuth.—When 2 pts. of tin are fused with 2 pts. bismuth and 1 pt. mercury, and the mixture pulverized after cooling, a *Mosaic Silver* is likewise obtained.

F. Amalgam of Tin and Zinc.—1 pt. zinc, 1 tin, and 2 mercury, form Kienmayer's amalgam, and 2 pts. zinc, 1 tin, and $3\frac{1}{2}$ to 6 mercury, form Singer's amalgam for the rubbers of electrical machines. The tin is first added to the melted zinc, and then the mercury poured in after the liquid is sufficiently cooled.

## Mercury and Lead.

A. Lead-amalgam.—Formed by triturating lead-filings with mercury, or by shaking mercury into melted lead. A bar of lead immersed for 10 days in cold mercury, appears thoroughly penetrated by the mercury, though it still remains somewhat ductile; it is also covered at the surface of the mercury with soft, feathery, silver-white crystals. (Daniell.) A bar of lead, bent in the form of a siphon, and dipping into mercury by one end, allows the mercury to flow out at the other and lower end, till the vessel is completely emptied. If the bar is made of non-hammered lead, the first drop of mercury shows itself in 24 hours; but if the lead has been hammered, it does not appear till after 10 days. The mercury does not pass along the bar, but through its pores. (Henry, *N. Bibl. univ.* 29, 175; also *Pogg.* 52, 187.) Sodium-amalgam immersed in a solution of acetate of lead, is converted into lead-amalgam. (Böttger.)

Solid lead-amalgam is tin-white, crystallo-granular, pulverizable, and fuses at a moderate heat. The crystals contain 2 pts. of lead and 3 of mercury.

1 volume of lead and 2 volumes of mercury form an amalgam which at 17° has a specific gravity of 12·8648; 1 vol. lead and 3 vols. mercury, sp. gr. 13·0397; and 1 vol. lead with 4 vols. mercury, sp. gr. 13·1581; condensation therefore takes place. (Kupffer.)

The solid amalgam, mixed with a larger quantity of mercury, forms a granular, pasty mixture of the solid and liquid amalgams, from which the latter may be pressed out between wash-leather; with a still larger quantity of mercury it forms a liquid. Both the paste and the liquid yield a black powder, when agitated in the air (according to Bonsdorff, only when the air is moist). According to Berzelius, this powder is a mixture of a very small quantity of suboxide of lead with a large quantity of unaltered amalgam. It is produced when only 1 grain of lead is dissolved in from 12 to 16 pounds of mercury. (Lucas.) The liquid compound behaves

with potassium-amalgam and water, just like a solution of tin and mercury. (Serullas.) Joule obtains $Pb^2Hg$ in the same manner as $Zn^2Hg$. (p. 125.)

B. Selenide of Mercury and Lead.—Laminar with the cleavage-planes of the cube, or granular and compact. Sp. gr. 7·3 (from 7·804 to 7·8765, according to H. Rose). Soft. Lead-grey. When heated in a glass tube closed at bottom, it forms a lead-grey sublimate, having the metallic lustre. (Zinken.) When the compound is thus treated, the selenide of mercury evaporates with ebullition, and the selenide of lead remains behind. (H. Rose.) Heated in a glass tube, open at both ends, it first yields the sublimate just mentioned—then, above that, a sublimate of mercuric selenite, which, when heated before the blowpipe with a very strong and long-continued blast, may be fused into transparent, yellow drops. When ignited with tin (or with carbonate of soda: *H. Rose*), it yields a sublimate of mercury. Decrepitates strongly before the blowpipe, and when carefully roasted, forms a deposit on the charcoal just like selenide of lead (V. 139); with fluxes it likewise behaves like that compound. (Zinken, *Pogg.* 3, 277.) Specimens from the same vein exhibit very different proportions of lead and mercury; when the mineral lies close to Bitter spar, it contains scarcely anything but selenide of lead; but as the specimens lie more remote from that formation, the quantity of selenide of mercury becomes greater. The two specimens on which the following analyses were made belonged to the same vein. (H. Rose, *Pogg.* 3, 297.)

| | At. | | | H. Rose. | | At. | | | H. Rose. |
|---|---|---|---|---|---|---|---|---|---|
| Pb | 3 | 312 | 54·55 | 55·84 | | 4 | 416 | 26·73 | 27·33 |
| Hg | 1 | 100 | 17·48 | 16·94 | | 7 | 700 | 44·99 | 44·69 |
| Se | 4 | 160 | 27·97 | 24·97 | | 11 | 440 | 28·28 | 27·98 |
| PbSe,HgSe | | 572 | 100·00 | 97·75* | | | 1556 | 100·00 | 100·00 |

* The loss is chiefly in the selenium. (H. Rose.)

The solution of iodide of lead in a hot solution of mercuric nitrate deposits nothing on cooling, but when evaporated, leaves a white powder, which is not decomposed by water, but dissolves almost completely. (Preuss, *Ann. Pharm.* 29, 328.)

C. Amalgam of Antimony and Lead. — Wetterstädt's *Marine Metal*, recommended for the sheathing of ships. A sample having a specific gravity of 11·204, contained 94·4 per cent. of lead, 4·3 antimony, and 1·3 mercury; another, of specific gravity 11·053, contained a somewhat larger quantity of antimony, and more than 0·75 per cent. mercury, which appeared to be situated chiefly at the surface. (J. L. Jordan, *J. pr. Chem.* 10, 439.)

D. Amalgam of Bismuth and Lead.—Pulverized lead-amalgam triturated with pulverized bismuth-amalgam, unites with it and forms a liquid amalgam (H. Davy), the combination being attended with great depression of temperature (Orioli, Döbereiner, I. 299.) *e. g.* 1 pt. lead, 1 bismuth, and 3 mercury. (H. Davy.)

E. Amalgam of Lead and Tin.—A bar of the alloy of lead and tin, immersed in cold mercury, is instantly penetrated by the mercury, and corroded at the lower part; it likewise becomes covered at the part near the surface of the liquid, with six-sided tables, some of which float on the

top. A crystal of a salt immersed in a watery liquid, is chiefly dissolved at the upper part, because the solution is heavier than the liquid; in this case, the contrary effect is produced, because the fluid amalgam of lead and tin is lighter than the mercury. (Daniell.)

F. Amalgam of Bismuth, Lead, and Tin.—*a.* Rose's fusible metal fused with $\frac{1}{16}$ pt. of mercury, liquefies at a temperature considerably below 100; *e. g.* a tea-spoon made of it melts when put into a cup of tea. When fused in a glass tube and immediately poured out, it leaves a specular film behind it. (Berzelius, *Lehrb.*)

*b.* Amalgam for injecting anatomical preparations: 20 pts. bismuth, 12 lead, 7 tin, and 4 mercury, (or more exactly: 497 pts. bismuth, 310 lead, 177 tin, and 100 mercury). Silver-white, solid at ordinary temperatures, becomes soft at 67·5°, melts at 77·5°, and does not solidify till cooled down to 60°. (Göbel, *Schw.* 48, 486.) Another recipe: 1 pt. bismuth, 1 lead, 1 tin, and a proportionate quantity of mercury.

*c.* Amalgam for silvering the inside of glass globes: 2 pts. bismuth, 1 lead, 1 tin, and 10 mercury. This amalgam hardens after a while.

## Mercury and Iron.

A. Iron-amalgam.—Combination between these metals is very difficult, and takes place under peculiar circumstances only; it is possible, indeed, that all the varieties of iron-amalgam hitherto obtained, may be mere mixtures of mercury with very finely divided iron.

1. Sodium-amalgam immersed in a saturated solution of green vitriol, is converted in a few minutes, into a silvery, tenacious mass, separate globules of which very readily obey the magnet; when exposed to the air, it quickly becomes covered with a yellow film of ferric oxide. The watery liquid above the amalgam thus formed, contains sulphate of soda, together with flakes of hydrated ferric oxide. (Klauer, *Ann. Pharm.* 10, 89.) When the amalgam is formed in this manner, with a mixture of 1 pt. sodium and 100 mercury, hydrogen gas is evolved; when the evolution of gas ceases, which it does after a few minutes, the formation of the amalgam is complete. In small globules, it is attracted by a strong magnet. When distilled, it leaves finely divided iron. When exposed to the air, it becomes covered with a blackish grey coating of oxide, but the decomposition is not completed till after a considerable time. When the amalgam is heated in contact with the air, and stirred at the same time, the iron burns in small glittering stars. (Böttger, *J. pr. Chem.* 1, 304.)—2. Zinc-amalgam formed of equal weights of mercury and zinc, is triturated with aqueous protochloride of iron, and the resulting mixture of iron and mercury kneaded together at a high temperature, till complete combination takes place. (Aikin, *Gilb.* 14, 242.)—3. One part of iron filings is intimately mixed with 2 parts of alum; 2 or 3 parts of mercury are then added; the whole triturated for an hour, at a gentle heat, with $\frac{1}{2}$ pt. of water; and the alum finally removed by washing with a larger quantity of water. This amalgam swells up after a while to double its original volume [from liberation of hydrogen?], and when it is pressed with the fingers, the bladders burst, and the mass becomes filled with cracks and small holes. When the amalgam is triturated with silver-glance or red silver-ore, the mercury is transferred to the silver. (Vogel, *Crell. Chem. Ann.* 1789, 2, 309.)—¶ 4. Joule (*Chem. Gaz.* 1850, 339)

obtains an amalgam having the composition FeHg, by the electrolysis of an iron solution, the negative pole being formed of mercury. ¶.

B. Iodide of Mercury and Iron.—Formed by evaporating a saturated solution of iodide of mercury in aqueous protiodide of iron, over oil of vitriol in vacuo; this mode of evaporation is rendered necessary by the great tendency of the solution to oxidate.—Yellowish-brown prisms, which, when exposed to the air, become covered with a red-brown powder. (Bonsdorff.)—The solution of iodide of mercury in hot aqueous iodide of iron deposits part of the iodide of mercury as it cools; the remaining liquid, evaporated till it forms a saline crust, yields brownish-yellow, very deliquescent needles, which are decomposed by a larger quantity of water, and dissolve in strong acetic acid and in alcohol. (Berthemot.)

C. Bromide of Mercury and Iron.—Turbid yellowish prisms, which quickly deliquesce when exposed to the air in its ordinary state. (Bonsdorff.)

D. Chloride of Mercury and Iron.—Aqueous protochloride of iron readily takes up corrosive sublimate, and first deposits a portion of that compound unaltered: but, afterwards, when evaporated over oil of vitriol, yields honey-yellow, rhombic prisms, isomorphous with those of the manganese salt, and therefore consisting of $FeCl, HgCl + 4$ Aq. They deliquesce in the air, with separation of a brown powder. (Bonsdorff.)

## Mercury and Cobalt.

A. Cobalt-amalgam.—1. Sodium-amalgam immersed in a saturated solution of chloride of cobalt, liberates hydrogen gas and precipitates protoxide of cobalt, converting the liquid into a violet-coloured magma, and at the same time takes up a portion of the cobalt. The amalgam is less fluid than mercury, and is not affected by the magnet till part of the mercury has been driven off by heat. (Böttger.)—2. An amalgam consisting of 1 pt. of zinc and 6 of mercury, immersed in an aqueous solution of chloride of cobalt supersaturated with ammonia, liberates a considerable quantity of hydrogen gas, and is converted into cobalt-amalgam, the zinc dissolving in the liquid. The liquid above the zinc-amalgam must be renewed as often as it loses its colour. The zinc still contained in the amalgam may be dissolved out by boiling dilute sulphuric acid, which does not act on the cobalt of the compound. The amalgam is of a dull silver-white colour, and is attracted by the magnet, even when not perfectly freed from zinc. When heated in a close vessel, it leaves the cobalt in the form of a grey magnetic mass. Exposed to the air, it becomes covered with a black powder of oxidized cobalt.—Aqueous chloride or sulphate of cobalt, yields the same amalgam, but not so quickly; from nitrate of cobalt the zinc-amalgam separates nothing but protoxide. (Damour, *J. pr. Chem.* 17, 346.)

B. Chloride of Mercury and Cobalt.—By dissolving corrosive sublimate in aqueous chloride of cobalt, and evaporating, carmine-coloured, highly deliquescent prisms are obtained, isomorphous with the corresponding manganese and iron salts. (Bonsdorff.)

## Mercury and Nickel.

A. Nickel-amalgam.—When sodium-amalgam is immersed in water saturated with chloride of nickel, and the liquid heated, hydrogen gas is evolved, hydrated oxide of nickel precipitated, and the sodium-amalgam converted into nickel-amalgam. This amalgam is almost as fluid as mercury. It is not magnetic, and causes no evolution of gas when immersed in water or in dilute acids. (Böttger, *J. pr. Chem.* 12, 351.)—2. On treating a nickel-solution in the manner described for the preparation of cobalt-amalgam, the same phenomena are produced. After a few days, when the amalgam no longer liberates hydrogen from fresh quantities of the ammonio-chloride of nickel, it is pulverized and boiled for a while with dilute sulphuric acid, till the greater part of the zinc has dissolved, with evolution of hydrogen. If the boiling be too long continued, the nickel likewise dissolves, fetid hydrogen gas being at the same time evolved.—The amalgam is solid, and may be attracted by the magnet. When distilled, it leaves metallic nickel in the form of an ash-grey, spongy mass. On exposure to the air, a black crust of oxidized nickel forms upon its surface till it is converted into running mercury. Cold dilute sulphuric or hydrochloric acid dissolves out the nickel from it very slowly,—the same acids, when hot, produce this effect somewhat more quickly. Nitric acid dissolves it completely. It may be combined with larger quantities of mercury. Aqueous chloride or sulphate of nickel may be substituted for the ammonio-chloride, but they form the amalgam less quickly; from nitrate of nickel, zinc-amalgam throws down nothing but hydrated oxide of nickel. (Damour.)

B. Chloride of Mercury and Nickel.—By spontaneous evaporation, small, apple-green, regular octohedrons are obtained, having probably a composition corresponding to that of chloride of mercury and calcium; and the mother-liquid, when evaporated over sulphuric acid, yields deliquescent oblique rhombic prisms. (Bonsdorff.)

## Mercury and Copper.

A. Copper-amalgam.—1. A piece of copper-foil immersed in a solution of nitrate of mercury, is gradually penetrated by the mercury, and at last becomes brittle.—2. The amalgam may be formed by triturating mercury with common salt and verdigris. (Lewis.)—3. By triturating 2 parts of mercury, $2\frac{1}{2}$ of verdigris, and 1 of common salt with a small quantity of heated vinegar, which must be renewed as it evaporates, and purifying the amalgam by washing. (Boyle.)—4. By mixing 1 part of finely divided copper—obtained by reducing the oxide with hydrogen, or by precipitation from the sulphate by zinc or iron—with a few drops of mercurous nitrate, by which it is quickened, and then triturating with 3 parts of mercury, a light red amalgam is formed. (Berzelius.)—5. Mercury placed in contact with the negative pole of a voltaic pile, and covered with solution of blue vitriol into which the positive wire dips, becomes perfectly saturated with copper. (Grove, *Phil. Mag. J.* 15, 83.) ¶ According to Joule, the amalgam thus obtained has the composition CuHg; and the same definite compound is obtained by dissolving copper in mercury, and removing the excess of the latter by strong

pressure. (*Chem. Gaz.* 1850, 339.) ¶—6. Sodium-amalgam immersed in a solution of blue vitriol, is converted into copper-amalgam. (Klauer.)—A strong solution of blue vitriol and sal-ammoniac, treated in a similar manner, yields a somewhat bulky amalgam of copper and ammonium, which has a reddish or golden-yellow colour, and soon decomposes.—7. Zinc-amalgam, immersed in a copper solution supersaturated with ammonia, forms an amalgam in white ramifications. (Damour.)

B. *Hyposulphite of Mercurous and Cuprous Oxide?*—When a solution of hyposulphite of mercuric oxide and potash is mixed with sulphate of cupric oxide, the liquid remains clear at first, but soon becomes turbid, and yields a brown-red precipate, which must be washed with cold water. Part of the excess of acid appears to be converted into sulphuric acid by reducing the protoxides of copper and mercury to dioxides. The precipitate heated out of contact of air, yields sulphurous acid, mercury, sulphide of silver, and sulphide of copper. It blackens when boiled with water, which dissolves sulphuric acid from it and forms sulphide of copper. Nitric acid extracts copper from it, with evolution of nitrous gas, and leaves a light yellow powder, consisting of sulphide of mercury combined with the nitrate and sulphate of mercuric oxide. Ammonia and potash blacken the precipitate when heated with it, and acquire a blue colour; with potash, however, the colour is but faint. (Rammelsberg, *Pogg*, 56, 319.)

| | | | Rammelsberg. |
|---|---|---|---|
| $5Cu^2O$ | 360 | 26·32 | 26·14 |
| $3Hg^2O$ | 624 | 45·61 | 45·60 |
| $8S^2O^2$ | 384 | 28·07 | 27·51 |
| KO | | | 1·02 |
| $5(Cu^2O,S^2O^2)+3(Hg^2O,S^2O^2)$ | 1368 | 100·00 | 100·27 |

C. Chloride of Mercury and Copper.—From a solution of corrosive sublimate in aqueous chloride of copper, the simple chloride of mercury separates first, and afterwards the double salt in needles united in radiated masses and permanent in the air. (Bonsdorff.)

D. Chloride of Mercury, Copper, and Potassium.—A dilute solution of mono-acid or bi-acid chloride of mercury and potassium (pp. 101, 102), mixed with chloride of copper and left to evaporate freely, yields crystals of the double salt now under consideration. Afterwards, either the double chloride of mercury and potassium, or the chloride of copper separates out, accordingly as the one or the other salt was in excess in the mixture. An excess of one of the salts is essential to the formation of good crystals of the double salt. (Bonsdorff.)

Right rhombic prisms. *Fig.* 75; also with the *p*- face instead of the *y*- faces $u' : u = 109° 23'$; $y : y$ backwards $= 70·5'$. (Nordenskiold.)—The crystals have a strong glassy lustre; their colour is between emerald-green and grass-green, and they yield a light green powder.—The salt fuses when heated, turns yellowish-brown, evolves water, and afterwards corrosive sublimate. Permanent in dry air, but turns yellowish in damp air from decomposition. In air saturated with moisture, it deliquesces and forms needles, probably consisting of chloride of mercury and potassium. The crystals, when immersed in cold water, to which they impart a light blue colour, acquire a white glimmering surface, probably in consequence of the formation of needles of the bi-acid chloride of mercury and potas-

sium. In boiling water they form a grass-green solution, and crystallize out from it unaltered when evaporated by the aid of heat; but, if the solution be rapidly cooled, the greater part of the chloride of mercury and potassium crystallizes out alone, and the liquid turns blue. The salt is affected in the same manner by hydrated alcohol at a boiling heat; absolute alcohol does not dissolve it. (Bonsdorff, 33, 81.)

| | *Crystallized.* | | Bonsdorff. *a.* | | *b.* |
|---|---|---|---|---|---|
| 3KCl | 223·8 | 31·28 | 31·48 | | 31·47 |
| 3HgCl | 406·2 | 56·78 | 56·95 | | 57·56 |
| CuCl | 67·4 | 9·42 | 9·32 | | 8·00 |
| 2HO | 18·0 | 2·52 | 2·25 | | 3·07 |
| 3(KCl,HgCl) + CuCl + 2Aq. | 715·4 | 100·00 | 100·00 | | 100·10 |

*a* was crystallized from a solution containing excess of chloride of copper; *b* from a solution containing an excess of chloride of mercury and potassium. (Bonsdorff.)

### Other Compounds of Mercury.

With Silver, Gold, Platinum, Palladium, Rhodium, Iridium, and Osmium.

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## Chapter XXXVII.

# SILVER.

Proust. *J. Phys.* 62, 211; also *N. Gehl.* 1, 508.

*Argentum, Luna, Diana, Argent, Silber.*

*History.* Silver has been known from the earliest times. The alchemists were acquainted with horn-silver and nitrate of silver.

*Sources.* Silver is tolerably abundant, and occurs: Native; as sulphide (Vitreous Silver or Silver-glance); as sulphide of silver and antimony (Brittle Silver-glance or Psaturose, Red Silver, and Miargyrite); as sulphide of silver and iron (Sternbergite); as sulphide of silver and copper (Argentiferous Copper-glance); as sulphide of antimony, silver, and copper (Polybasite); as sulphide of antimony, silver, and lead (Donacargyrite); and in some other sulphur-salts (Fahl-ore, Graugültigerz, Weissgültigerz); as selenide of silver and copper (Eukairite); as iodide of silver; as bromide; as chloride (Horn-silver); as chloro-bromide; as antimonide of silver; as telluride of silver; as telluride of gold and silver

(White Tellurium and Graphic Tellurium); as silver-amalgam; as an alloy of silver and copper; and as an alloy of gold and silver.

¶ According to Malaguti, Durocher, and Sarzeaud (*N. Ann. Chim. Phys.* 28, 129), a small quantity of silver occurs in sea-salt, in sea-water itself (about 1 milligramme in 100 litres); in various fuci (*Fucus serratus* and *F. ceramoïdes* contain at least $\frac{1}{100000}$); in chemical products for the preparation of which common salt is used (*e.g.* carbonate of soda and hydrochloric acid); in the ashes of land plants, the insoluble portion containing more silver than the soluble part; in the ash of ox-blood, in rock-salt, and probably also in coal. In sea-water it occurs in the form of chloride. ¶

*Preparation.*—1. The silver is first made to unite with lead, and the lead, together with other foreign matters, is afterwards removed.—*a.* Rich ores are fused with lead in crucibles. Two layers then form, the upper one consisting chiefly of silver and lead, the lower of sulphide of lead and other metallic sulphides.—*b.* The silver ores are fused in a smelting furnace, and the melted mass as it flows out, is stirred up with melted lead. In this case, also, the silver unites with part of the lead, while the rest of that metal mixes, in the form of sulphide, with the sulphides of the other metals contained in the ore.—*c.* The silver ores are fused with roasted lead ores, which may likewise contain silver, and with artificially prepared oxide of lead, such as litharge (V. 106, 2, *a*).—*d.* The silver ores are fused with unroasted lead-glance and with iron: this is called the *method of precipitation* (V. 106, 2, *b*).—*e.* Very poor silver ores are fused with iron pyrites, and the argentiferous sulphide of iron thus obtained, is first roasted, and then smelted with lead ores, the lead separated from which, takes up the silver.—*f.* Argentiferous copper ores are treated as described on page 398, vol. v., so as to yield argentiferous blue copper; and this, when fused with three times its weight of lead, and left to cool in the pans, solidifies in cakes, which are a mixture of two alloys. On the application of a gentle heat, the alloy which contains the larger quantity of lead, and nearly all the silver, flows out; and the remainder of the cake, which is contracted and porous, and contains a small quantity of lead and a very small quantity of silver united with the copper, yields, when heated to redness in contact with the air, a number of products, among which is a small quantity of lead containing silver and copper.

The argentiferous lead obtained by either of these processes, is strongly heated in a reverberatory furnace, the hearth of which is covered with lime and washed wood-ashes, the flame being made to play over it. The lead, together with any other base metals accidentally present, is oxidized by the air blown over its surface by means of two pair of bellows, and forms at first a comparatively impure, difficultly fusible oxide, the *dross*,—but afterwards a continually purer oxide, which partly flows off in the form of litharge, and partly sinks into the hearth. The silver separated by this refining process, is called in German, *Blicksilver.* —The silver, often mixed with gold, remains behind in the metallic state, and is freed from the last traces of foreign metals by again fusing it in the air. This process yields *Fine silver* or *Cupelled silver.*—If the argentiferous lead be left to solidify slowly after fusion, lead nearly free from silver crytallizes out first, and may be removed by a ladle, while nearly all the silver remains in the portion (amounting to half or a third of the whole), which remains longest in a state of fusion. (Pattinson, *Jahresber*, 17, 111.)—¶ Two new methods of extracting silver from its ores, without

the aid of mercury, have lately been introduced in Mexico. The first of these methods consists in roasting the ores with common salt; dissolving the resulting chloride of silver by means of a hot solution of common salt; and precipitating this solution with metallic copper.—According to the second method, the ores are converted into sulphates by roasting; the sulphates extracted with water; and the solution likewise precipitated by copper. (Liebig & Kapp's *Jahresber*, 2, 629.)—Malaguti and Durocher (*Compt. rend.* 29, 735) find that silver may be directly reduced from the sulphide, without previous conversion into chloride, by subjecting the ores to the action of nascent hydrogen, or, still better, by treating them with metallic copper and blue vitriol, green vitriol, and alum. ¶

2. The silver is first united with mercury and then separated from that compound: *Amalgamation.*—*a.* Ores which only contain metallic silver are agitated with mercury, after being finely divided by stamping. —*b.* Ores in which the silver exists in the form of sulphide, require a previous treatment with chlorine-compounds, to convert the sulphide of silver into chloride. It is then reduced by iron or another metal.— *a. Freiberg Process.* The ore is finely pounded, intimately mixed with common salt, and roasted—whereby metallic silver, chloride of silver, and sulphate of soda are produced—and afterwards worked about in casks with water and iron, or other base metals, and finally also with mercury, which takes up the silver. The mercury is separated from the silver by pressing out the excess, which contains but little silver, and distilling the solid amalgam in an apparatus very similar to that which is used at Horzowitz (p. 2). The porous silver which remains is freed from any baser metals that may be mixed with it, by cupellation with lead or by ignition in the air, and subsequent treatment with dilute sulphuric acid. (Lampadius.)—*β. American Process.* The ore in a finely divided and moist condition, is exposed for a considerable time to the successive action of common salt, sulphate of copper, and mercury. To effect an intimate mixture of the ore with these materials, men or horses are made to walk about for several hours on the heaps of moistened ore, which are formed on a paved floor, and the whole is frequently stirred with shovels. The sulphate of copper used is generally roasted copper pyrites, known by the name of *Magistrat;* the mixing of this substance with ore already containing common salt is called the *Incorporation.* Finally, the silver-amalgam formed by the previous processes is separated from the exhausted ore by washing with water in casks. (Lyon, *Schw.* 54, 1.) In this process, the common salt and the sulphate of copper form sulphate of soda and protochloride of copper. The latter gives up chlorine, and converts part of the sulphide of silver into chloride, separating the sulphur, provided that an excess of common salt is present, to hold in solution the dichloride of copper as it forms. The latter then acts upon another portion of the sulphide of silver, forming disulphide of copper and chloride of silver. The chloride of silver thus produced dissolves in the common salt, and is decomposed by the mercury subsequently added, yielding silver and calomel. This process is always attended with a loss of mercury, which, however, may be diminished by the addition of iron previously to the mercury. (Boussingault, *Ann. Chim. Phys.* 51, 337.)

Might not many of the poorer silver-ores be treated as follows: pounding them finely—roasting them, if they contain sulphur—and heating them with a quantity of oxide of manganese and hydrochloric acid sufficient to convert the sulphide of silver into chloride—washing

thoroughly with water—dissolving out the chloride of silver by ammonia—separating it by distillation—and reducing with sulphuric acid and iron? (Gm.)

¶ Malaguti and Durocher have examined the influence of the accompanying matrix and of the soluble salts on the amalgamation of silver ores. They find that the matrix exerts a greater disturbing effect on the process, in proportion as it is fatter and more argillaceous, and less, as it is poorer and more siliceous. They attribute a peculiar deteriorating effect to carbonate of lime, and foreign metallic sulphides (PbS, ZnS, &c.); the presence of salts (common salt among the rest) they regard, on the other hand, as advantageous. From a series of comparative experiments, they conclude that when mercury alone is used, chloride of silver is more difficult to reduce than metallic silver, and even than the sulphide; but that the process is greatly accelerated by metallic iron. The extreme slowness of the American amalgamation process they attribute to the presence of foreign metallic sulphides, the sulphide of silver being converted into chloride less quickly than most of the other sulphides. Moreover, this conversion of the sulphide of silver is exclusively due to the chloride of copper (the sulphur being either separated in the free state or converted into sulphuric acid, according to the facility of access of the air), the common salt merely serving to accelerate the action. (*Compt. rend.* 29, 735; Liebig & Kopp's *Jahresber.* 2, 631.) [For Percy's experiments on the separation of silver and gold from their ores in the wet way, *vid. Phil. Mag. J.* [3], 36, 1.] ¶

*Purification.* 1. By repeated cupellation with pure lead.

2. The silver is dissolved in nitric acid, common salt added to throw it down as chloride, and the metal separated from that compound after careful washing with hot water.—*a.* A crucible is nearly filled with an intimate mixture of 3 pts. chloride of silver and 1 pt. common resin; a gentle heat applied at first, whereupon the resin burns with a flame coloured green by the hydrochloric acid formed from the chlorine of the horn-silver and the hydrogen of the resin; the heat is then raised to the melting-point of the silver, a small quantity of borax being added, and a few slight blows given to the crucible to accelerate the union of the silver. The charcoal which remains on the top is perfectly free from silver; this process is preferable to all the rest. (Mohr, *Ann. Pharm.* 3, 331.)—*b.* The chloride of silver is ignited with a fixed alkali.—*a. With hydrate of potash;* this, however, is rarely used.—*β. With* 1 *or* 2 *pts. of dry carbonate of soda.* Oxygen and carbonic acid are then given off with effervescence. (Gm.)

$$AgCl + KO,CO^2 = Ag + KCl + O + CO^2.$$

The chloride of silver fuses before it is decomposed, and then sinks into the pores of the earthen crucible, thereby causing a loss; this loss may be more or less prevented by the following methods: An intimate mixture of 1 pt. chloride of silver and 1 pt. carbonate of potash or $\frac{2}{3}$ pt. dry carbonate of soda is placed in a glass vessel, which is carefully heated to low redness in a crucible filled with sand; the contents are then washed with water, and the silver is obtained in the form of a soft powder. This process is dangerous, from the liability of the glass to crack.—The mixture is placed in an earthen crucible, and the temperature kept for the first half-hour at low redness, so that the greater part of the gases are

given off before the mass fuses and spits; after which, a stronger heat is applied. The bottom and sides of the earthen crucible are thickly covered with 1½ pt. moist carbonate of potash—the heat raised to redness—and the dry mixture of equal parts of chloride of silver and carbonate of potash introduced by small portions at a time. (Gm.)—Between 1 and 2 pts. of carbonate of potash are fused in the crucible, and the thoroughly dried chloride of silver then introduced in successive small portions. A loss of 2 or 3 per cent. by spitting is scarcely to be avoided. (Giese, *Scher. Ann.* 3, 141.) A mixture of carbonate of soda with the carbonate of potash is useful, because it lowers the melting-point. (Mohr.)—In every case, the mixture is strongly ignited at last, to bring about the union of the separated silver.—The silver reduced by this process sometimes retains a small quantity of chloride, which remains behind when the silver is dissolved in nitric acid. (Proust.)—*γ. With lime.*—100 pts. of chloride of silver, 20 of dried lime, and 4·2 of charcoal. (Gay-Lussac, *Ann. Chim. Phys.* 14, 319.) With these proportions, great loss is incurred. (Trommsdorff, *N. Tr.* 5, 2, 437.) 1 pt. of chloride of silver with 1½ to 2 pts. lime, fuses imperfectly, and produces but an incomplete separation of the silver. (Meissner, *Berl. Jahrb.* 1818, 178.)—*c.* The chloride of silver is boiled with strong caustic potash, and the resulting oxide of silver, after being washed and dried, is fused till the silver melts together. For this purpose, the chloride of silver precipitated by common salt is well washed with water by decantation, the liquid being frequently stirred with a glass rod, and then, while still moist, boiled in a clean vessel of platinum, silver, or iron, with excess of potash-ley of specific gravity at least 1·25, stirring well all the time, till a sample of the oxide taken out and washed, dissolves completely in nitric acid. The oxide is then washed by decantation, first three times with hot water, and then with cold water, because, when nearly washed, it has a tendency to rise to the surface of the hot water. The oxide, if pure, is heated alone till it is reduced to the metallic state; if it still contains chloride of silver, a small portion of carbonate of potash is added. The quantity of chloride still present being but small, there is no fear of loss from its sinking into the crucible, or by spitting. (W. Gregory, *Phil. Mag. J.* 22, 284.)—*d.* The chloride of silver is placed in contact with iron or zinc and water, to which, in order to accelerate the action, a small quantity of hydrochloric or sulphuric acid may be added; and the reduced silver is quickly washed, first with acidulated and afterwards with hot pure water, and then fused with borax and nitre. Silver precipitated by zinc presents the appearance of a soft grey powder. Giese decomposes 1 part of chloride of silver with 1 part of zinc, 2 parts of oil of vitriol, and 6 of water; with these proportions, the whole of the zinc dissolves. Iron-wire may also be used for the same purpose. Or the chloride of silver may be heated in an iron vessel with iron filings and water, and a small quantity of hydrochloric acid. (Lesage.)—It is not easy to obtain a complete decomposition with zinc; moreover, a small quantity of that metal unites with the silver, and cannot be removed by hydrochloric acid—so likewise do some of the impurities of the zinc or the iron. (Gregory.) The chloride of silver may also be decomposed by trituration with twice its weight of mercury and a small quantity of water, the resulting amalgam ignited after washing with water, and the residual silver formed into a button by fusion with $\frac{1}{10}$ of its weight of borax.—*e.* A cylinder, open at top, closed at bottom with a piece of membrane, and containing water in which finely divided chloride of silver is diffused,

is placed upon a zinc plate immersed in water, and a connexion made by means of a silver or platinum wire, between the zinc plate and the water of the cylinder. (Fischer, *Schw.* 20, 48.) This decomposition takes about a week, and is only adapted for small quantities. (Giese.)

3. The impure silver is dissolved in nitric acid, the dilute solution precipitated by copper; and the precipitated silver, after thorough washing, is digested with ammonia as long as that liquid acquires a blue colour; or it is left for some time in contact with an aqueous solution of silver-nitrate, in order to dissolve the copper that is mixed with it, and then washed and ignited. When a solution of silver-nitrate is precipitated by green vitriol, the silver precipitate contains sulphate of ferric oxide (or sulphate of ferric oxide and silver-oxide, according to Giese), which remains behind in the form of a yellow powder when the silver is dissolved in nitric acid.

*Properties.* Silver crystallizes naturally in forms belonging to the regular system. Fig. 1, 2, 3, 4, 9, and 11 (with octohedral faces). Macle-crystals of cubes and leucite-octohedrous also occur; dendritic forms are likewise frequent. It is harder than gold, but softer than copper; elastic; gives a clear ringing sound; is very malleable and ductile; may be hammered into leaves, 0·00001 of an inch in thickness. One grain of silver may be drawn out into a wire 400 feet long. Fracture indented. Specific gravity of fused silver 10·4382 (Karsten), 10·474 (Brisson), 10·481 (Fahrenheit), 10·53 (G. Rose); of hammered silver, 10·510 (Brisson), 10·50 (Muschenbroek), 10·57 (G. Rose); of silver precipitated from the nitrate by green vitriol, from 10·56 to 10·92 (G. Rose). Silver is the whitest of all the metals.

In the finely-divided state, *e.g.* as obtained in the decomposition of the chloride by zinc in the humid way, silver presents the appearance of a dull, dark grey powder. To obtain it in this form, the chloride must not be precipitated at a high temperature, or washed with water at a temperature above 60°, or dried by the aid of heat; neither must the silver precipitated by zinc be subjected to heat in either of these ways. If a higher temperature is applied, the silver becomes more compact, whiter, and more metallic. (Berzelius.) Silver precipitated on glass in very thin films (by aldehyde-ammonia), or thrown down from a liquid in the form of a very fine powder, exhibits a violet colour by transmitted light.

Silver may be welded. Pulverulent silver reduced from the chloride by zinc may be welded by the process devised by Wollaston for platinum. (Fournet, *Ann. Chim. Phys.* 75, 435.) Fuses at 999° (C. Prinsep), at 1000° (Pouillet), at 1034° (Guyton-Morveau), at 1223° (Daniell), and in the fused state exhibits a stronger lustre. According to Persoz (*Chim. molecul.* 240), pieces of solid silver float upon the melted metal, showing that silver expands in solidifying, like water.

Silver in the melted state absorbs oxygen in the same loose manner as water takes up various gases. This effect takes place when the silver is fused in the air, or under a small quantity of nitre. The absorbed oxygen escapes as the silver solidifies, and may be collected over water. If, in consequence of rapid cooling, the surface of the silver solidifies before the oxygen has escaped from the interior, the gas bursts the superficial crust, and drives out part of the fused silver in spherules and excrescences; this effect is called the *spitting* of silver. Charcoal powder thrown on melting silver withdraws the absorbed oxygen, and consequently prevents the silver from spitting as it cools. (Samuel Lucas,

*Ann. Chim. Phys.* 12, 402; also *Schw.* 53, 187; also *N. Tr.* 4, 2, 81.) ¶. According to H. Rose (*Pogg.* 68, 274), the spitting of silver takes place not only in contact with the air, but also under layers of various salts an inch thick, sufficient, therefore, to prevent access of atmospheric oxygen; in this case, however, the salt must contain a substance which does not give up oxygen till raised to a very high temperature; moreover, the saline covering must consist of easily fusible salts, which do not solidify till after the silver. No spitting takes place when silver is fused under common salt; but on the addition of nitre, spitting is produced. Chlorate of potash, however, does not produce this effect, because it gives up the whole of its oxygen before the silver melts. These facts will serve to explain why it is that no spitting takes place in the reduction of silver by carbonate of potash. For the evolution of oxygen takes place at a temperature below that at which silver melts; and the reduced porous metal does not fuse till the heat is considerably increased; but it then finds no more oxygen in the fused chloride of potassium to combine with, and the oxygen of the air is completely kept off by the saline crust. Spitting is also not produced under very viscid saline crusts, even when a sufficiency of oxygen is present. ¶ 8 grammes of silver fused in the air give off 0·0078 litre of oxygen in solidifying; but the presence of 5 per cent. of copper deprives the silver of the power of absorbing oxygen. (Chevillot, *Ann. Chim. Phys.* 13, 299; also *Schw.* 53, 190.) When small quantities of nitre are thrown on melted silver at intervals, for half an hour, and the crucible is then placed under a bell-jar filled with water, the silver gives off 22 times its volume of oxygen gas, and acquires a rough, wrinkled surface. [Might not part of the oxygen here evolved proceed from peroxide of potassium?] When oxygen gas is passed for half an hour over melted silver contained in a porcelain tube, the tube closed, and then left to cool, a vacuum is first formed in the tube (rendered evident by the rising of the liquid which closes it), but afterwards, as the silver solidifies, a large quantity of oxygen is evolved. When silver fused in the air is dropped into water, every drop gives off large bubbles of oxygen gas. A small quantity of copper diminishes the absorption of the oxygen, and 2 or 3 per cent. stops it completely; lead and gold act in the same manner. (Gay-Lussac, *Ann. Chim. Phys.* 45, 221.) Silver at a white heat decomposes aqueous vapour passed over it, liberating a small quantity of hydrogen and taking up oxygen, whereby it acquires the property of spitting.

Silver boils only at the temperature produced by a burning mirror or by oxygen gas; it then rises in white fumes. In an open crucible it volatilizes gradually, even at an incipient white heat, losing about 1 per cent. in an hour; not, however, if it be covered with charcoal dust. (Lampadius, *J. pr. Chem.* 16, 204.)

## *Compounds of Silver.*

### Silver and Oxygen.

#### A. *Suboxide of Silver.* $Ag^2O$?

1. A solution of silver-oxide in aqueous ammonia deposits, on exposure to the air, a suboxide which exhibits a grey colour and strong lustre by reflected light, and when in thin layers, a bright yellow by transmitted light; it contains 108 silver to 5·4 oxygen, and when heated,

fuses, gives off oxygen, and is converted into metallic silver. (Faraday, *Quart. J. of Sc.* 4, 268; also *Ann. Chim. Phys.* 9, 107.)

2. The oxalate, mellitate, and citrate of silver-oxide, heated to 100°, or a little higher, in a current of hydrogen gas, are reduced to yellow or brown salts of the suboxide. The dark wine-red solution of citrate of suboxide of silver in water yields, with potash, a black precipitate, which, after drying, acquires the metallic lustre by pressure. When heated, it is resolved into oxygen gas and metallic silver; with oxygen-acids, it is resolved into the oxide which dissolves, and metallic silver which remains behind. With hydrochloric acid it yields a brown powder, probably consisting of dichloride of silver; *q.v.* (Wöhler, *Ann. Pharm.* 30, 1; also *Pogg.* 46. 629.)

## B. Silver-oxide. $AgO$.

*Formation.* 1. Silver does not oxidise either in dry or in moist air at any temperature below its boiling point; but when heated to that temperature in the air on charcoal by oxygen gas, or in Marcet's blowpipe, or the oxy-hydrogen blowpipe, it burns with a greenish light, depositing a brown powder on glass held over it. Silver-leaf made to close the circuit of the voltaic battery, or a wire through which the charge of a strong electric battery is passed, likewise burns with a greenish light.—2. Silver decomposes oil of vitriol at the boiling heat, nitric acid at ordinary temperatures. It is less oxidized than platinum by fusion in the air in contact with nitre or with caustic potash.—3. Silver dissolves in a boiling solution of ferric sulphate, the product being ferrous sulphate and silver-sulphate, but separates out again in the metallic state on cooling; so that the ferric sulphate is reproduced:

$$Fe^2O^3,3SO^3 + Ag = 2(FeO,SO^3) + AgO,SO^3.$$

(*Sch.* 94.). If the air be not excluded, part of the silver remains in solution when the liquid is cooled, especially when a large quantity of free sulphuric acid is present; for part of the ferrous sulphate produced at the higher temperature is converted—with especial rapidity when the acid is in excess—into ferric sulphate, and can therefore no longer contribute to the precipitation of the silver on cooling. Moreover, ferric sulphate, even in the cold, dissolves a small quantity of silver, which may be precipitated by common salt or green vitriol. The solution of the silver is particularly rapid and abundant when excess of sulphuric acid is present; for the ferric oxide, which has given up oxygen to the silver, then takes it up again with greater facility from the air. (Wetzlar, *Schw.* 53, 94.) The silver which is precipitated on cooling is contaminated with basic sulphate of ferric oxide. The supernatant liquid contains ferric oxide, ferrous oxide, and silver-oxide in solution, and therefore yields a black precipitate with ammonia; blue, with ferricyanide of potassium; and white, with common salt. (A. Vögel, *J. pr. Chem.* 20, 362.)

*Preparation.*—1. By precipitating an aqueous solution of silver-nitrate with potash or baryta-water free from hydrochloric acid, washing the precipitate, and drying it at a gentle heat.—2. By boiling recently precipitated and still moist chloride of silver with excess of caustic potash, of sp. gr. from 1·25 to 1·3, and then washing and drying. (Gregory.)—The chloride of silver must not be triturated in the mortar, because it then aggregates in lumps, and becomes more difficult to decom-

pose. The boiling must be continued till a sample taken out and washed dissolves completely in nitric acid; if this should not take place after ten minutes' boiling, the potash-ley must be poured off, the oxide triturated in a mortar—which may now be done without injury—and again boiled for five minutes, either with the old or with fresh potash-ley. In some cases, it is necessary to decant the liquid yet once more, again triturate the oxide, and boil a third time. The oxide is then washed three times by decantation with boiling water, then repeatedly with cold water, and lastly on the filter. (Gregory.)

*Properties.*—The oxide prepared by (1) is a brown powder, which when dried between 60° and 80° becomes nearly black; its specific gravity is 7·143 (Herapath), 7·250 (P. Boullay), 8·2558 (Karsten), it has a disagreeable metallic taste. (Proust, Bucholz.) When prepared by (2) it forms a soft, black or bluish-black powder. (Gregory.)

| | | Berzelius. | | | Thomson. |
|---|---|---|---|---|---|
| | | earlier. | later. | latest. | |
| Ag | 108 | 93·103 | 93·075 | 93·103 | 93·112 | 93·2 |
| O | 8 | 6·897 | 6·925 | 6·897 | 6·888 | 6·8 |
| AgO | 116 | 100·000 | 100·000 | 100·000 | 100·000 | 100·0 |

| | H. Davy. | Gay-Lussac. & Thénard. | Val. Rose. | Proust. | Bucholz. | Kirwan. |
|---|---|---|---|---|---|---|
| Ag | 93·1 | 92·937 | 91·38 | 91·33 | 90·9 | 90·25 |
| O | 6·9 | 7·063 | 8·62 | 8·67 | 9·1 | 9·75 |
| AgO | 100·0 | 100·000 | 100·00 | 100·00 | 100·0 | 100·00 |

Decomposed by light or at a red heat into oxygen gas and metallic silver. Hydrogen gas reduces it to the metallic state, even at 100°. (Wöhler, *Ann Pharm.* 30, 4.)—Gives up its oxygen to aqueous phosphorous acid. In the recently precipitated state, it is decomposed by aqueous sulphurous acid, yielding metallic silver and soluble sulphate of silver-oxide; but the decomposition is not complete, even when heat is applied. (A. Vogel.) Under water it is reduced by zinc, cadmium, tin, and copper, but not by iron or mercury. (Fischer, *Pogg.* 10, 605.)—In aqueous hypochlorous acid, it yields chloride of silver, oxygen gas, and a small quantity of chlorine. (Balard.)

*Combinations.* *a.* With Water.—*Aqueous Silver-oxide.*—The oxide is slightly soluble in water, and imparts to it a metallic taste (Bucholz, *Beitr.* 2, 5), and alkaline reaction (Fischer, *Kastn. Arch.* 9, 356.) The solution acquires a reddish colour when exposed to light, is rendered turbid by a small quantity of carbonic acid, and recovers its clearness on the addition of a larger quantity of that acid. (Wetzlar, *Schw.* 53, 102.)

*b.* With Acids, forming the Salts of Silver-oxide, or Silver-salts.—The affinity of silver-oxide for acids is greater than that of cupric oxide or zinc-oxide. The silver-salts are prepared by dissolving the metal in oxidating acids, such as sulphuric or nitric acid, or by double decomposition. Silver-salts are generally colourless, unless they contain a coloured acid. The soluble salts do not redden litmus provided the acid is saturated; they have a strongly metallic taste, and act as acrid poisons. Those which contain volatile acids give them up at a red heat, and leave metallic silver; with carbonate of soda before the blowpipe, they all yield a metallic globule. With borax and microcosmic salt, they behave like oxide of silver.

The following substances precipitate silver from its solution in the metallic state: *Phosphorus.*—A dilute solution of the nitrate is more rapidly reduced by this substance than a strong solution. Liquid sulphide of phosphorus throws down an olive-green, non-metallic powder. (Boeck.) Phosphoric oxide, on the contrary, throws down phosphide of silver and phosphate of silver-oxide. (Dulong.) The precipitation takes place in the cold, and without evolution of hydrogen. (Wurtz.) *Phosphorous acid.*—Characters traced on paper with a solution of silver become metallic in a bottle containing phosphorus and atmospheric air. (Grotthuss.)—*Phosphuretted hydrogen* gas:

$$8(AgO,NO_5) + PH_3 = 8Ag + PO_5 + 3HO + 8NO_5.$$

The bulky precipitate which this gas produces in a solution of nitrate or sulphate of silver-oxide is brown at first, but consists of metallic silver, and gradually assumes a metallic aspect; the liquid contains phosphoric acid. (H. Rose, *Pogg.* 14, 184; 24, 318).—*Sulphurous acid.* This substance forms with silver-solutions a white precipitate, which turns grey on boiling; the remaining liquid, which still contains sulphurous acid, becomes turbid repeatedly when left to stand for some time, and yet retains silver in solution; the precipitated silver is generally mixed with sulphide. (A. Vogel, *J. pr. Chem.* 29, 279.)—Sulphite of ammonia throws down white sulphite of silver-oxide, which becomes covered, slowly at ordinary temperatures, but quickly on the application of heat, with a silver-shining film of metal. Sulphurous acid throws down white flakes, which soon turn yellowish, afterwards brown, and then contain sulphide of silver. A similar precipitation is produced by sulphite of potash, which, however, besides the white flakes, which afterwards turn brown, likewise produces black metallic-looking laminæ of sulphide of silver. (Pleischl, *Zeitschr. Phys. v. Wiss.* 3, 106.)—*Zinc, cadium, tin, lead, iron, manganese, copper, mercury, bismuth, tellurium, antimony, arsenic.*—Lead and tin precipitate the nitrate solution most quickly; then follow the other metals in this order: cadmium, zinc, copper, bismuth, antimony, arsenic, mercury. (Fischer, *Pogg.* 6, 43.)—*Zinc* immersed in a slightly acidulated silver-solution, becomes covered, from the beginning to the end of the precipitation, with black, moss-like silver, containing zinc; the deposit, however, assumes a lighter colour towards the edges, and, when detached by gas-bubbles, parts with the zinc which it contains, and turns white, but resumes its dark colour if again brought in contact with the zinc. If a neutral solution of silver be used, only the portions first precipitated are black; the subsequent portions are continually lighter in colour. (Wetzlar, *Schw.* 50, 98).—According to Fischer, on the contrary, neutral solutions are disposed to yield alloys from beginning to end of the precipitation; acid solutions, on the contrary, only towards the end. —If the silver solution contains copper, the silver is nevertheless precipitated free from copper, the latter metal not being reduced till after the silver. (Fischer.)—Zinc reduces nitrate of silver-oxide in the dry state, and likewise in the state of aqueous or alcoholic solution,—also the aqueous sulphate, and the carbonate and phosphate when immersed in water. (Fischer.) *Cadmium* reduces the same silver-salts as zinc. (Fischer.)—*Tin*, immersed in an aqueous solution of silver-nitrate, throws down black metallic silver, together with a brown powder, at the same time colouring the liquid brown. From the alcoholic solution of the nitrate, tin precipitates but a small quantity of silver, and only on first immersion. It reduces the dry nitrate of silver oxide, the aqueous solu-

tion of the sulphate, and the carbonate and phosphate immersed in water. (Fischer.)—*Iron* reduces the aqueous solution of the sulphate, and the carbonate and phosphate immersed in water. It does not reduce the alcoholic nitrate, and in an aqueous solution of that salt, reduction takes place only where the iron projects above the liquid,—or when it is dipped into an acid solution, then taken out and exposed to the air till it has become covered with ferrous nitrate, and again immersed. At a boiling heat, the aqueous nitrate is easily reduced by iron. (Fischer, Brandenburg; *comp.* I. 370....372)—*Manganese* reduces silver but very slightly from the solution of the nitrate. (Fischer.)—*Tellurium* acts very freely on the solution, and forms a black powder, which does not assume the metallic lustre under pressure. (Fischer.)—*Bismuth* reduces the nitrate of silver-oxide dissolved in water or alcohol, and the carbonate when immersed in water, but not the aqueous sulphate. (Fischer.)—*Antimony* reduces only the aqueous nitrate and the carbonate immersed in water, not the alcoholic nitrate or the aqueous sulphate. (Fischer.)—*Arsenic* reduces the aqueous and alcoholic nitrate.—*Copper* exerts a reducing action on the nitrate, both in the dry state and when dissolved in water or alcohol—on the aqueous solution of the sulphate, and on the carbonate and phosphate immersed in water. (Fischer.) Silver precipitated by copper from the nitrate is pure at first, but the portions last thrown down are contaminated with copper, proceeding from galvanic action; the copper, however, redissolves on immersion for some time in a solution of silver-nitrate. (Gay-Lussac, *Gilb.* 72, 326.)—*Mercury*, immersed in an aqueous solution of the nitrate or sulphate of silver-oxide throws down an amalgam of silver. From the alcoholic solution, it precipitates a black powder containing suboxide of silver; it also exerts a slight action on the carbonate and phosphate. (Fischer.)—Brass and the alloys of silver with zinc, tin, and lead, likewise reduce silver-salts completely; palladium exerts no reducing action. (Fischer; *vid.* Fischer, *Gilb.* 72, 289; *Pogg.* 6, 43; 8, 488; 10, 607; 12, 503; 16, 126.)—[For the action of metals upon chloride of silver, chromate of silver-oxide, and the ammoniacal solutions of silver, *see* these compounds.]—*Uranous oxide.*—This oxide, prepared according to the second process described on page 159, vol. iv,—but not that which is prepared by the third process—decomposes a solution of silver-nitrate without any evolution of gas, producing metallic silver and uranic nitrate. (Ebelmen, *N. Ann. Chim. Phys.* 5, 219);

$$AgO,NO^5 + 2UO = Ag + U^2O^3,NO^5.$$

*Hydrated Manganous oxide.* (Schnaubert, *Von der Verwandtschaft*, pp. 103, 106.)—Alkalis added to a mixed aqueous solution of a silver-salt und a manganous salt, throw down a black mixture of silver and peroxide of manganese, which dissolves in acids, reproducing a silver-salt and a manganous salt. (Wöhler, *Pogg.* 41, 344.)—*Ferrous Sulphate.*—From an aqueous solution of nitrate or sulphate of silver-oxide, green vitriol throws down a greyish-white, pulverulent precipitate of metallic silver (Keir), which redissolves on boiling. (Proust, Bucholz; *comp.* p. 139.) The precipitation is incomplete; a silver-solution mixed with green vitriol, and separated from the precipitated silver, still yields a precipitate of chloride of silver with common salt, and likewise a precipitate of metallic silver on further addition of green vitriol. (Wetzlar.) The precipitated silver is mixed with basic sulphate of ferric oxide, which remains behind on dissolving the silver in nitric acid. (Gièse, A. Vogel.)—*Protochloride of Tin.*—The solution of this substance added in

small quantity to a silver-solution, throws down chloride of silver, which, on further addition of the tin-salt, is converted into brownish black, pulverulent metallic silver.—*Organic Compounds.*—A solution of silver-nitrate, mixed with either volatile oils or charcoal, and exposed to sunshine or raised to a boiling heat, yields a precipitate of metallic silver. (Rumford, *Scher. J.* 2, 3.) Boeck did not succeed in producing the precipitation by charcoal at a boiling heat. Sugar, at a boiling heat, throws down a black powder, which appears to be a mixture of the metal and the oxide. (A. Vogel.)—Tincture or infusion of galls (which does not act in the cold) yields on boiling, or after long standing, a black powder consisting of metallic silver. (Proust.)—¶ Many organic substances mixed with ammonio-nitrate of silver, throw down metallic silver in the form of a beautiful specular film lining the sides of the vessel; this effect is produced by aldehyde, saccharic acid, salicylous acid, and pyromeconic acid, and by various essential oils. Of the last-named substances, a mixture of oil of cinnamon and oil of cloves is found to produce by far the most brilliant speculum, and has lately been brought into use for silvering mirrors, in place of the ordinary process with tin and mercury; this process is particularly well adapted for curved surfaces. Grape-sugar likewise produces a very fine specular silvering in the course of 6 or 12 hours in the cold, but in 2 or 3 minutes on the application of heat; the colour of the speculum is, however, darker than that produced by aldehyde, or by the mixed oils just mentioned. Cane-sugar also produces a mirror with the aid of heat, but not without. Gum-arabic and starch produce a strongly coloured mirror after long boiling; phloridzine and salicine produce a similar effect. Oil of turpentine and bay-oil likewise produce specular deposits, but only from very strong solutions, and after a long time; resin of guiacum acts in a similar manner. Of the two oils composing the oil of Jamaica pepper, the one which is heavier than water, and possesses acid properties, produces a specular film equalling in beauty that which is produced by the mixed oils of cloves and cinnamon; the lighter oil, which is neutral, does not reduce silver, even after long boiling. The cinnamic, benzoic, meconic, comenic, tannic, gallic and pyrogallic acids, the resins of benzoin, elemi and olibanum, and oil of rosewood, and glycerine, were found by Stenhouse not to produce specular deposits. (*Ann. Pharm.* 54, 102.)—Bolley (*Jahrb. f. Pharm.* 18, 384) finds that silver is easily thrown down from cupriferous solutions of its salts by cane-sugar, on the addition of caustic ammonia or potash, and the application of heat. The precipitate, which is metallic, may be washed first with hot water, and then with hot acetic acid. ¶

Hydrosulphuric acid and alkaline hydrosulphates, added to silver-solutions, throw down the whole of the silver in the form of a brownish-black sulphide. This precipitation takes place equally well if the silver-solution is previously saturated with ammonia. The precipitate is insoluble in ammonia and in alkaline hydrosulphates. It shows itself down to the 20,000th degree of dilution of the silver-salt (Pfaff); in a solution containing 1 part of silver in 35000 parts of the solution. (Harting, *J. pr. Chem.* 22, 52.)—The recently precipitated sulphides of manganese, cadmium, iron, cobalt, and nickel, likewise throw down sulphide of silver from silver-salts. (Anthon, *J. pr. Chem.* 10, 353.)—Hydriodic acid and aqueous metallic iodides throw down all the silver in the form of a pale yellow iodide. The precipitate is curdy when formed in strong solutions; in a dilute solution it merely produces an opalescence. Its colour deepens slowly when exposed to light. It is but very

sparingly soluble in excess of iodide of potassium, and not sensibly soluble in ammonia—which, however, turns it whiter—or in dilute nitric acid. The reaction with iodide of potassium has its limit in a solution containing 1 part of silver-oxide in 30,000 parts of liquid. (Harting.) 1 part of iodide of potassium dissolved in 500 parts of water, gives a yellow precipitate with silver-nitrate; in 5000 water a yellowish-white precipitate; in 50,000 water, a white turbidity; and in 500,000 water, a scarcely perceptible opalescence. (Baumann, *N. Br. Arch.* 29, 214.)—Iodine likewise produces this precipitate. Hydrobromic acid and aqueous metallic bromides throw down all the silver as a yellowish white bromide. This precipitate dissolves very sparingly in dilute, but freely in concentrated ammonia.—Hydrochloric acid and aqueous metallic chlorides precipitate the silver completely in the form of chloride from all silver-salts excepting the hyposulphite. The precipitate is curdy when formed in strong solutions, but in case of great dilution, it shows itself as a milky opalescence in the liquid. It turns violet when exposed to light. It dissolves very easily in dilute ammonia, sparingly in concentrated hydrochloric acid, and not at all in nitric acid. The opalescence shows itself, even when the silver-nitrate is 120,000 times diluted (Pfaff); with 1 pt. silver-oxide in 240,000 pts. of liquid. (Harting, *J. pr. Chem.* 22, 52.) In a solution containing 1 pt. of silver in 200,000 parts, hydrochloric acid or common salt produces a very slight turbidity; if the solution contains only 1 pt. of silver in 400,000, the same reagents produce a scarcely perceptible opalescence, and if the proportion of liquid amounts to 800,000, the opalescence does not show itself for a quarter of an hour. (Lassaigne, *J. Chim. Méd.* 8, 583.)—1 part of common salt dissolved in 100,000 parts of water, still forms a cloud in a silver-solution. (Bostock, *N. Gehl.* 4, 551.)—Chlorine likewise produces this precipitate. All insoluble silver-salts are converted into chloride of silver by immersion in aqueous solutions of metallic chlorides; if, however, they have been thoroughly dried, the change is not complete for several days. (Fischer, *Schw.* 53, 486.)

A very small quantity of ammonia forms, with perfectly neutral silver-salts, a slight white turbidity, and a white granular precipitate, which turns black on exposure to light, and dissolves in a larger quantity of ammonia, forming a clear solution. Acid silver-solutions form a perfectly clear mixture with ammonia in all proportions. A silver-solution supersaturated with ammonia, gives a white precipitate with potash. (H. Rose.)—All fixed alkalis throw down from silver-salts the brown oxide of silver. If the fixed alkali is contaminated with a metallic chloride, the precipitated silver-oxide will also be contaminated with chloride of silver.—Monocarbonate or bicarbonate of potash or soda forms a white precipitate of carbonate of silver-oxide; so likewise does carbonate of ammonia, an excess of it, however, redissolving the precipitate.—Ordinary phosphate of soda gives a yellow precipitate with silver-salts, according to Pfaff, down to the 10,000th degree of dilution.—Pyrophosphate and metaphosphate of soda precipitate them white.—Iodate and bromate of potash form white precipitates with silver-salts. Both these precipitates are easily soluble in ammonia.—Chromate of potash throws down, from not very dilute solutions of silver-salts, a dark purple-red precipitate of chromate of silver-oxide.—Arsenite of potash throws down egg-yellow arsenite of silver-oxide. A solution containing 1 part of silver-oxide in 6000 parts of liquid, still gives a perceptible yellow pre-

cipitate, and the reaction reaches its limit with 1 pt. of silver-oxide in 20,000 parts of liquid. (Harting.)

Oxalic acid throws down, from silver salts, a white, pulverulent oxalate of silver-oxide. Hydrocyanic acid and metallic cyanides precipitate cyanide of silver, curdy in strong solutions, and producing an opalescence in the liquid when very dilute. Sulphocyanide of potassium forms a white precipitate of sulphocyanide of silver. Ferrocyanide of potassium forms a white, and ferricyanide of potassium a red-brown precipitate.—All silver-salts which are insoluble in water, dissolve in nitric acid and in ammonia.—Silver-oxide forms double salts with many other salifiable bases, especially with ammonia.

*c.* With Ammonia, forming *Berthollet's Fulminating Silver.*

## C. *Peroxide of Silver ?*

First noticed by Ritter.—Deposited on the positive platinum wire when aqueous nitrate of silver-oxide is placed in the voltaic circuit. The silver-solution must be concentrated, otherwise nothing but oxygen is obtained at the positive pole; but even when a concentrated solution is used, oxygen gas is still evolved, so that, especially towards the end of the process, the quantity of silver deposited in the form of peroxide at the positive pole is not so great as that which is reduced at the negative pole. Grove's battery yields the peroxide more rapidly than an ordinary voltaic battery of 60 pairs; but the latter deposits it in a more distinctly crystalline form. (R. Wallquist, *J. pr. Chem.* 31, 179.)

Brittle, iron-black octohedrons, united in a series of prisms and needles (Wallquist); apparently tetrahedrons. (Grotthuss, *Gilb.* 61, 60; and *Schw.* 28, 324.)

Decrepitates in the flame of a candle and leaves metallic silver. (Grotthuss.) Detonates strongly when struck in contact with phosphorus or sulphur. (Grotthuss.) Aqueous hydrochloric acid converts it, with momentary evolution of chlorine, into chloride of silver. (Ritter.) With aqueous hypochlorous acid, it yields chloride of silver, oxygen gas, and a small quantity of chlorine. (Balard.) In a solution of sal-ammoniac, it evolves gas and forms chloride of silver, part of which dissolves; and with a boiling solution (not with a cold solution) of common salt, it forms chloride of silver and free soda, the action being attended with evolution of gas. (Fischer.) It dissolves in aqueous ammonia with rapid evolution of nitrogen, forming argentate of ammonia. (Grotthuss.) Phosphoric and sulphuric acid dissolve it, with gradual evolution of oxygen, forming ordinary silver-salts. In nitric acid it dissolves unaltered.

It was at one time universally supposed that this so-called peroxide of silver contained only silver and oxygen; and Wallquist quite recently believed that he had determined its composition by analysis to be 87·23 per cent. silver, and 12·77 oxygen, giving the formula $AgO^2$; Fischer, however, has obtained the following very different results regarding it.

The peroxide prepared from nitrate of silver-oxide always contains nitric acid, and consequently, when heated, gives off yellow vapours with slight detonation; moreover, when pulverized and thoroughly washed with cold water, it still gives up nitrate of silver-oxide to hot water, but retains the property of giving off yellow vapours when heated. Similarly, the peroxide prepared from sulphate of silver-oxide, retains a portion of sulphuric acid; acid phosphate of silver-oxide, and likewise the acetate,

do not yield peroxide of silver in the voltaic circuit. The peroxide obtained from the sulphate is not distinctly crystalline. and does not decrepitate in the flame of a candle; in other respects, it is similar to that prepared from the nitrate. The amount of silver in the peroxide is not so great as that given by Wallquist, who probably did not heat it strongly enough to decompose the nitrate. (Fischer, *Kastn. Arch.* 16, 215; also *J. pr. Chem.* 32, 108.)—Fischer's statement, so far as it relates to peroxide of silver obtained from the nitrate, is confirmed by the observations of Gmelin. The needles, washed with water till the liquid gave no turbidity with hydrochloric acid, and after drying, gently heated in a white flask, gave off nitrous fumes, and cold water extracted from the residue, a large quantity of silver-nitrate. May not the crystals consist of nitrate peroxide of silver?

## Silver and Carbon.

A. Carbide of Silver.—*a.* $Ag^2C$.—Silver, fused for three-quarters of an hour with lamp-black, takes up about 3 per cent. of carbon. (Gay-Lussac, *Ann. Chim. Phys.* 58, 223.)—*b.* AgC.—Remains in the form of a dull, yellow residue, containing 94·48 p. c. silver, and 5·52 carbon, when cuminate of silver-oxide is heated to redness in an open vessel; it undergoes no alteration by continued ignition. Dilute nitric acid dissolves it with separation of charcoal. (Gerhardt & Cahours.)—2. When dicyanide of silver is strongly ignited, there remains a dull white, fused carbide of silver, the carbon of which burns only at the surface on ignition in contact with the air; when dissolved in nitric acid, it leaves a network of pure charcoal. (Liebig & Redtenbacher, *Ann. Pharm.* 38, 129.)—*c.* $AgC^2$.—Aqueous pyroracemate of silver-oxide, heated for a long time in the water-bath, gives off carbonic acid, and deposits a grey powder, which acquires metallic lustre when rubbed on the burnishing stone; and after being well boiled with carbonate of potash, then washed with water and ignited in the air, leaves a residue containing 10·51 p. c. of carbon, and 89·49 of silver. The same salt when subjected to dry distillation, yields a grey carbide of silver, having the metallic lustre, and containing more than $1\frac{1}{2}$ At., but less than 2 At. carbon to 1 At. silver. (Berzelius, *Pogg.* 36, 28.)—2. Maleate of silver-oxide, heated till it deflagrates, leaves a grey, metallic carbide of silver, which may be freed from oily matter by washing with water containing caustic potash, and then with water acidulated with hydrochloric acid, and from chloride of silver by ammonia. By ignition in the air, it is converted into pure silver, amounting to 90·072 per cent. Nitric acid dissolves it, with separation of black flakes of charcoal. (Regnault, *Ann. Pharm.* 19, 153.)

B. Carbonate of Silver-oxide, or Silver-carbonate.—The statement of Selb, that this salt occurs in nature, has been disproved by Walchner. (*Mag. Pharm.* 25, 1.)—Oxide of silver absorbs carbonic acid from the air during washing and drying. (Fisher, *Kastn. Arch.* 9, 346.)—The salt is prepared by precipitating nitrate of silver-oxide with monocarbonate or bicarbonate of potash or soda, washing the precipitate with cold water, and drying it in the shade. The precipitate is white at first, but when the soluble salts are washed out, it assumes a yellow colour. When carbonate of potash is mixed with excess of a strong solution of silver-nitrate, the yellow precipitate is obtained at once. (Fischer.)

Yellow powder, of a paler colour than the phosphate. (Wetzlar, *Schw.* 53, 100.) Specific gravity, 6·0766. (Karsten.)—Blackens readily when exposed to light, or when gently heated. (Fischer.) Easily converted into chloride of silver by aqueous hydrochloric acid or by dissolved metallic chlorides. (Wetzlar.)

| | | | | | Setterberg. |
|---|---|---|---|---|---|
| AgO | 116 | .... | 84·06 | .... | 84·02 |
| $CO^2$ | 22 | .... | 15·94 | .... | 15·90 |
| HO | | .... | | .... | 0·08 |
| $AgO,CO^2$ | 138 | .... | 100·00 | .... | 100·00 |

The salt examined by Setterberg was precipitated, either hot or cold, by bicarbonate of potash.

## Silver and Boron.

Borate of Silver-oxide, or Silver-borate.—*Monobasic.*—Formed by precipitating a moderately dilute solution of silver-nitrate with a saturated solution of borax. The precipitate obtained is exactly the same, whether the borax be poured into the silver solution, or the latter into the borax, and whether the borax has or has not been previously ignited. If the solution be very dilute—for instance, if the saturated solution of borax be diluted with 30 or 40 times its weight of water, its mixture with the silver-solution remains clear at first, and, even when the silver-salt is in excess, gradually deposits pure brown oxide of silver. Borate of potash, both in the state of concentrated and of dilute solution, produces the same reactions as borax under similar circumstances. Borate of ammonia, in the state of strong solution, produces a precipitate of borate of silver-oxide; but in the dilute state, it does not throw down the pure oxide.—White flakes, converted by drying into a white powder, which turns violet, and afterwards black when exposed to light, fuses at a gentle heat, and dissolves, without decomposition, in a considerable quantity of water. (H. Rose, *Pogg.* 19, 153.) Sexborate of potash likewise produces a white precipitate, soluble in a larger quantity of water. (Laurent, *comp.* Tunnermann, *Kastn. Arch.* 20, 28.)

| | | | | | H. Rose. | |
|---|---|---|---|---|---|---|
| AgO | 116·0 | .... | 76·92 | .... | 76·5 to 77·71 | |
| $BO^3$ | 34·8 | .... | 23·08 | .... | 23·5 ,, 22·29 | |
| $AgO,BO^3$ | 150·8 | .... | 100·00 | .... | 100·0 | 100·00 |

## Silver and Phosphorus.

A. Phosphide of Silver.—1. Formed by fusing 1 pt. of silver with 2 parts of glacial phosphoric acid and ½ pt. charcoal.—2. By throwing phosphorus on melted silver. As the mixture solidifies, phosphorus is set free, and afterwards takes fire. (Pelletier.)—3. By fusing 12 parts of triphosphate of silver-oxide ($3AgO,PO^5$) with 1 part of charcoal, at a moderate red-heat. (Landgrebe, *Schw.* 60, 128.)—The statement of Thomson and Landgrebe (*Schw.* 55, 96), that phosphide of silver may be precipitated from a solution of the nitrate by phosphuretted hydrogen, appears, according to H. Rose's experiments (p. 141), to be doubtful.

By 1 and 2: White, granular, semicrystalline; may be cut with the knife, and breaks to pieces under the hammer. Contains 20 per cent. of

phosphorus, which it gives off entirely when ignited in contact with the air. (Pelletier.)—When prepared by the third process, it forms a loosely-aggregated, brittle mass, which is easily cut with the knife, exhibits a silvery lustre when rubbed with a file, and contains 33·23 per cent. of phosphorus, of which it is partially deprived by fusion before the blowpipe, and completely by fusion with carbonate of soda. (Landgrebe.)

B. Phosphate of Silver-oxide, or Silver-phosphate.—*a. Triphosphate.*—Silver-oxide, agitated with aqueous diphosphate of soda, deprives it of part of its phosphoric acid. (Wetzler, *Schw.* 53, 100.)—The salt is prepared by precipitating nitrate of silver-oxide with diphosphate of ammonia, potash, or soda. The supernatant liquid contains free nitric acid. (Berzelius, Mitscherlich.)

$$3(AgO,NO^5) + 2NaO,cPO^5 = 3AgO,cPO_5 + 2(NaO,NO^5) + NO^5.$$

(*Schw.* 49.) If triphosphate of soda be used as the precipitant, the supernatant liquid remains neutral. (Graham.)

$$3(AgO,NO^5) + 3NaO,cPO^5 = 3AgO,cPO^5 + 3(NaO,NO^5).$$

The precipitate carries down with it a small portion of silver-nitrate, which cannot be completely removed by washing; hence, it gives off a small quantity of nitrous fumes when heated. (Graham, *Pogg.* 32, 45.)—Yellow powder, having a specific gravity of 7·321 at 7·5°. (Stromeyer.) After drying, it is perfectly anhydrous (Stromeyer), or contains only $\frac{1}{2}$ per cent. of water. (Berzelius.) Assumes a red-brown colour whenever it is heated. Fuses at a red-heat like horn-silver. (Berzelius.) According to Stromeyer, it does not fuse even at a strong red-heat; but in the blowpipe-flame, it melts into a dark brown liquid, which, on cooling, solidifies in a yellow mass. When kept for a considerable time in a state of fusion, it is partly converted into pyrophosphate [with reduction of silver?], and is thereby rendered more fusible and paler. If heated in the inner cone of a spirit-flame, it even becomes white on the surface after cooling. (Stromeyer, *Schw.* 58, 126.)—The salt blackens on exposure to light. It dissolves readily in aqueous phosphoric, nitric, or acetic acid, and in pure ammonia or carbonate of ammonia; less easily in nitrate and succinate of ammonia; and imperfectly in sulphate of ammonia. The solution of the salt in nitric acid yields crystals of silver-nitrate, and may be regarded as a mixture of that salt and free phosphoric acid. (Süersen, *Scher. J.* 8, 120.)

| | | | | | Berzelius. | | Stromeyer. |
|---|---|---|---|---|---|---|---|
| 3AgO..... | 348·0 | .... | 82·97 | .... | 82·975 | .... | 83·455 |
| $cPO^5$ ..... | 71·4 | .... | 17·03 | .... | 17·025 | .... | 16·545 |
| $3AgO,cPO^5$ | 419·4 | .... | 100·00 | .... | 100·000 | .... | 100·000 |

*b. Acid Phosphate.*—The yellow solution of the salt *a* in aqueous phosphoric acid. When evaporated, it first yields crystalline grains, which appear to consist of the salt *a*; then, if left to spontaneous evaporation, it deposits white, feathery crystals, which appear to be the diphosphate ($2AgO,HO,cPO^5$), but are immediately converted into the salt *a* by contact with water. A solution of silver-nitrate mixed with a large quantity of ordinary phosphoric acid, still yields these crystals on evaporation at a gentle heat. (Berzelius, *Ann. Chim. Phys.* 2, 163.)

¶. Schwarzenberg did not succeed in obtaining crystals by this process; but on evaporating the solution to a syrupy consistence, and mixing

it with ether, great heat was evolved, and a white crystalline powder separated, which was washed with absolute alcohol, to remove the free phosphoric acid adhering to it. It blackened on exposure to light, and was decomposed by water, yielding the yellow triphosphate and free phosphoric acid. It gave no water at 100°, but at 170° evolved 2·87 per cent. of water, and was converted into the pyrophosphate.

| | | | *dried at* 100°. Schwarzenberg. |
|---|---|---|---|
| 2AgO..... | 232·0 | 74·26 | 73·45 |
| HO ..... | 9·0 | 2·88 | 3·03 |
| $PO^5$ ..... | 71·4 | 22·86 | 23·52 |
| $2AgO,HO,PO^5$.... | 312·4 | 100·00 | 100·00 |

The salt probably still contained free phosphoric acid. (Schwarzenberg, *Ann. Pharm.* 65, 162.) ¶.

C. Pyrophosphate of Silver-oxide, or Silver-pyrophosphate.—*a. Bibasic.*—Formed by precipitating nitrate of silver-oxide with dipyrophosphate of soda. The supernatant liquid is neutral. (Clark, *Schw.* 57, 421.):

$$2(AgO,NO^5) + 2NaO,bPO^5 = 2AgO,bPO^5 + 2(NaO,NO^5).$$

At the first instant of precipitation, the precipitate appears to contain combined water, but soon parts with it. (Stromeyer.) Nitrate of silver-oxide added to an aqueous mixture of ordinary phosphate and pyrophosphate of soda, throws down first the yellow salt, and afterwards the white. (Stromeyer.)

White powder, of sp. gr. 5·306, at 75°; contains no water. Fuses somewhat below a red-heat, without any decomposition, and forms a dark brown liquid, which on cooling, solidifies in a white, radiated mass. Assumes a reddish colour on exposure to light. When boiled with ordinary diphosphate of soda, it is immediately decomposed, yielding ordinary yellow triphosphate of silver-oxide, and aqueous pyrophosphate of soda. [Probably in this manner ?

$$3(2AgO,bPO^5) + 2(2NaO,cPO^5) = 2(3AgO,cPO^5) + 2(NaO,bPO^5) + 2NaO,bPO^5.$$

According to this, the water should contain both monopyrophosphate and dipyrophosphate of soda.] The salt dissolves readily in cold nitric acid; but when boiled with either nitric or sulphuric acid, it is converted into the ordinary phosphate, so that the solution gives a yellow precipitate on the addition of ammonia. Aqueous hydrochloric acid converts it into chloride of silver and free phosphoric acid. It dissolves with tolerable facility in ammonia, and is thrown down unchanged by acids. Insoluble in acetic acid, and not altered by boiling with water. (Stromeyer, *Schw.* 58, 126.) Insoluble in solutions of the pyrophosphates; very slightly soluble in silver-nitrate. (Schwarzenberg.)

| | | | Berzelius. | Stromeyer. | Schwartzenberg. |
|---|---|---|---|---|---|
| 2AgO..... | 232·0 | 76·47 | 76·35 | 75·39 | 76·23 |
| $bPO^5$ ..... | 71·4 | 23·53 | 23·65 | 24·61 | 23·77 |
| $2AgO,bPO^5$ ..... | 303·4 | 100·00 | 100·00 | 100·00 | 100·00 |

D. Metaphosphate of Silver-oxide, or Silver Metaphosphate.—*a. Sesquibasic.*—The monobasic metaphosphate of silver-oxide *b*, immersed in boiling water, while recently precipitated and still moist, or the powder

introduced into cold water, and gradually raised to the boiling heat, fuses quickly into a grey viscid mass, having the consistence of turpentine, and capable of being drawn out into threads; it must be washed with cold water. A small quantity of the monobasic salt remains undecomposed in the middle of the mass; the hot water, when poured off and evaporated, deposits a white crystalline crust of monobasic salt. The salt is solid after cooling, and fuses alone less easily than under water. It is gradually decomposed by the continued action of boiling water. (Berzelius, *Pogg.* 19, 331.)

| | | | | | Berzelius. |
|---|---|---|---|---|---|
| 3AgO | 348·0 | .... | 70·90 | .... | 69·58 |
| $2aPO^5$ | 142·8 | .... | 29·10 | .... | 30·42 |
| $3AgO,2aPO^5$ | 490·8 | .... | 100·00 | .... | 100·00 |

*b. Monobasic.*—Formed by mixing a solution of silver-nitrate with an aqueous solution of recently ignited phosphoric acid, prepared with ice-cold water (Berzelius), or with a solution of mono-metaphosphate of soda. (Graham.) The gelatinous flakes must be washed with a small quantity of cold water. The white, pulverulent salt becomes soft and semi-fluid at 100°, and at a somewhat higher temperature, fuses into a transparent and colourless liquid, which on cooling solidifies in the form of a crystalline glass, and then flies to pieces. Cold water slowly takes up part of its acid, but boiling water slowly resolves it into an acid solution and the salt *a*. (Berzelius.)

| | | | | | Berzelius. |
|---|---|---|---|---|---|
| AgO | 116·0 | .... | 61·90 | .... | 64·52 |
| $aPO^5$ | 71·4 | .... | 38·10 | .... | 35·48 |
| $AgO,aPO^5$ | 187·4 | .... | 100·00 | .... | 100·00 |

As the salt had lost some of its acid during washing, it gave rather too much oxide of silver by analysis. (Berzelius.)

¶. A crystallized metaphosphate, containing 2 At. water of crystallization to 3 At. base and 3 At. acid, has been obtained by Fleitmann and Henneberg, by mixing the solution of the corresponding soda-salt with a very large excess of silver-nitrate. When this salt is fused, the water escapes with intumescence.

| | | | | | Fleitmann & Henneberg. |
|---|---|---|---|---|---|
| 3AgO | 348 | .... | 59·80 | .... | 58·62 |
| $3aPO^5$ | 216 | .... | 37·11 | .... | 38·21 |
| 2HO | 18 | .... | 3·09 | .... | 3·17 |
| $3(AgO,aPO^5)+2Aq.$ | 58·2 | .... | 100·00 | .... | 100·00 |

The salt does not alter in weight when left over sulphuric acid. When heated in the water-bath it gives discordant results, in consequence of a peculiar decomposition which it undergoes; for when about half the water has gone off, the salt acquires an acid reaction, becomes soft, and on subsequent exposure to the air, takes up more than 3 per cent. of water, which it gives up again at 100°, appearing to be thereby converted into the ordinary metaphosphate *b*. This salt is distinguished by the great permanence of its solution in cold water. It may be obtained in crystals from a solution strongly acidulated with nitric acid. In preparing this compound, it is necessary to use a very large excess of the silver-nitrate; otherwise crystals are obtained, consisting of a double metaphosphate of silver-oxide and soda. (Fleitmann & Henneberg, *Ann. Pharm.* 65, 310.)

According to Fleitmann, silver-oxide fuses very easily with excess

of phosphoric acid, forming a clear glass, from which a crystalline salt slowly separates on cooling. This salt consists of small shining, crystalline scales, perfectly insoluble in water. When treated with sulphide of sodium, they yield ordinary deliquescent metaphosphate of soda. (*Ann. Pharm.* 72, 246.) ¶.

*Acid Metaphosphate.* — 1. The aqueous solution produced by boiling the salt *b* with water.—2. Silver-crucibles in which phosphoric acid is fused are attacked by it, phosphide of silver and acid phosphate of silver-oxide being produced. (Bucholz.)

Fleitmann and Henneberg have likewise obtained the compounds $6AgO,4PO^5$ and $6AgO,5PO^5$, by double decomposition with the corresponding soda-salts. (*Ann. Pharm.* 65, 330.)

## Silver and Sulphur.

A. Sulphide of Silver.—Occurs in nature in the form of *Silver-glance.* Formed by heating silver-plates arranged in alternate layers with sulphur, or by fusing silver with potash-liver of sulphur, and exhausting with water. Precipitated in black-brown flakes on treating silver-oxide or silver-salts with hydrosulphuric acid or alkaline hydrosulphates. Obtained by Becquerel in octohedrons by the galvanic process (I. 402.) Forms the yellow, and afterwards brown film, with which silver vessels become tarnished when exposed to the sulphurous exhalations proceeding from the human body, from sewers, &c. (Proust.) The native sulphide crystallizes in the forms shown in figures 1, 2, 3, 4, 5, 8, 10, and 11. Sp. gr. 7·0. The artificially prepared sulphide has a density of 6·8501. (Karsten.) Both the natural and artificial varieties are malleable, of a blackish grey colour, and very fusible.

| | | | Vauquelin. | | Berzelius. | | Wenzel. | Klaproth. *native.* |
|---|---|---|---|---|---|---|---|---|
| Ag | 108 | 87·097 | 87·27 | | 87·032 | | 85·5 | 85 |
| S | 16 | 12·903 | 12·73 | | 12·968 | | 14·5 | 15 |
| AgS | 124 | 100·000 | 100·00 | | 100·000 | | 100·0 | 100 |

When heated in the air, it is resolved into sulphurous acid gas and metallic silver; when it is roasted at a gentle heat, a small quantity of sulphate is likewise produced. (Larranaga, *Gilb.* 22, 304.) When fused with iron, it yields sulphide of iron and metallic silver; with lead, the products are sulphide of lead and an alloy of lead and silver. Heated to redness in hydrogen gas, it forms sulphuretted hydrogen and metallic silver. (H. Rose.) Heated to redness in a current of aqueous vapour, it yields sulphuretted hydrogen, and becomes partially covered with metallic silver. (Regnault.) Not decomposed by chlorine gas in the cold, very slowly when heated. (H. Rose, *Pogg.* 42, 540.) In this reaction, 100 parts of sulphide of silver yield 115·43 chloride [or 124 yield 143·13]. (Fellenberg, *Pogg.* 50, 72.) Dissolves in tolerably strong sulphuric acid, with separation of sulphur. Not decomposed by aqueous protochloride of copper. (Boussingault.) If, however, the copper-solution contains common salt, the sulphide of silver becomes converted into chloride of silver and sulphide of copper. 100 parts of sulphide of silver treated in this manner for a few days, yield 146 parts of a mixture of chloride of silver and sulphide of copper. In the first instance, half of the sulphide of silver acts

upon the protochloride of copper, forming chloride of silver, free sulphur, and dichloride of copper, which remains dissolved in the common salt:

$$AgS + 2CuCl = AgCl + S + Cu^2Cl.$$

Afterwards, the dissolved dichloride of copper and the other half of the sulphide of silver, form chloride of silver and disulphide of copper:

$$AgS + Cu^2Cl = AgCl + Cu^2S.$$

Hence, sulphide of silver likewise undergoes decomposition in a solution of dichloride of copper in common salt. (Boussingault, *Ann. Chim. Phys.* 51, 350.) [The calculation given by Boussingault for the latter half of this reaction leads to the supposition that protosulphide of copper is produced together with the chloride of silver, although disulphide of copper must nevertheless be formed.] Sulphide of silver is insoluble in aqueous ammonia. It is only when precipitated in company with chloride of silver, that it partly dissolves together with the latter. (Gredy, *Compt. rend.* 14, 757.) It is insoluble in aqueous sulphurous acid (Berthier), and in solution of mercuric nitrate (Wackenroder).

B. Hyposulphite of Silver-oxide, or Silver-hyposulphite.—When a dilute neutral solution of silver-nitrate is dropped by small quantities at a time into dilute hyposulphite of potash, the white turbidity at first produced disappears again on agitation; as the quantity of silver-solution is increased, grey flakes are produced, and the supernatant liquid acquires a very sweet taste, arising from dissolved hyposulphite of silver-oxide, and is no longer precipitable by common salt, but gives a precipitate with sulphuretted hydrogen. When a still larger quantity of the silver-solution is added, the precipitate suddenly turns brown, and is afterwards converted into black sulphide of silver; and the supernatant liquid no longer tastes sweet, but gives a precipitate with common salt. If the solution of hyposulphite of potash be mixed at once with the quantity of silver-solution required to decompose it, the precipitate, which is white at first, soon passes through pale yellow, greenish yellow, yellowish brown, and red-brown, into the brown-black colour of sulphide of silver. A solution of the potash-salt, which contains only 1 pt. of hyposulphurous acid in 97·800 of water, still assumes a brown tint in a few minutes, when mixed with a solution of silver.

The salt is prepared by adding a moderately dilute solution of silver to an excess of tolerably concentrated hyposulphite of potash—washing the precipitated grey mixture of hyposulphite and sulphide of silver with cold water on a filter—extracting the hyposulphite of silver-oxide with ammonia—precipitating it from the solution by exact neutralization with nitric acid—and drying it as quickly as possible by pressure between paper. Snow-white powder, having a sweet taste. Slightly soluble in water. (Herschel, *Edinb. Phil. J.* 1, 26; 2, 154.) Easily decomposed into sulphuric acid and sulphide of silver. (H. Rose.):

$$AgO,S^2O^2 = AgS + SO^3.$$

Hyposulphite of silver-oxide combines with other hyposulphites, forming *Double Silver-hyposulphites.* The hyposulphites of silver-oxide and the alkalis are obtained by dissolving one of the following substances in an alkaline hyposulphite: viz. hyposulphite of silver-oxide, or the pure oxide (in which case a portion of the alkali is set free), or a salt of silver-oxide, or chloride of silver, in which cases, another alkali-salt is formed at

the same time. These salts may be precipitated from their aqueous solutions by alcohol, and washed with the latter liquid. They taste very sweet, and are decomposed by a moderate heat; hence they must be dried in vacuo over oil of vitriol at ordinary temperatures. (Herschel.)

¶ B′. Pentathionate of Silver-oxide.—Nitrate of silver-oxide, added to a solution of pentathionic acid, forms a yellow precipitate, which soon turns black from decomposition. (Kessler, vid. II, 164.) ¶

C. Tetrathionate of Silver-oxide.—Tetrathionic acid forms, with solution of silver, a white precipitate, which in a few seconds turns yellow and then black. (Fordos & Gélis.)

D. Trithionate of Silver-oxide.—The yellowish white precipitate produced by trithionic acid, quickly turns black in consequence of the formation of sulphide of silver and sulphate of silver-oxide. (Langlois.)

E. Sulphite of Silver-oxide, or Silver-sulphite.—Formed by precipitating a solution of the nitrate by aqueous sulphurous acid, not in excess, or by an alkaline sulphite. Even the free acid throws down nearly all the silver. (Berthier.)—An excess of the acid exerts a decomposing action (Muspratt), and the precipitate is converted into metallic silver when left for a long time in the liquid, or immediately on boiling. (H. Rose, *Pogg.* 33, 240.) An excess of the alkaline sulphite would redissolve the precipitate. (H. Rose.)—White granular precipitate. (Berthier.) It resembles chloride of silver, contains no water, and has an unpleasant taste. (Muspratt, *Ann. Pharm.* 50, 286.)—The salt, when exposed to the air [and light?], becomes dark purple, and afterwards black. (Muspratt.) When heated to 100°, either alone or under water, it is resolved in sulphate of silver-oxide and metallic silver. (Berthier.) [At the same time, perhaps, sulphurous acid is set free:

$$2(AgO,SO^2) = Ag + AgO,SO^3 + SO^2].$$

The decomposition is quicker and more complete if the water contains a small quantity of sulphite of potash. (Berthier.) Even the presence of sulphurous acid in the water favours the decomposition. (Muspratt.) The salt gives off sulphurous acid at a temperature short of commencing redness, and leaves a residue of silver, together with sulphate of silver-oxide, which, at a higher temperature, is resolved into silver, oxygen gas, and sulphurous acid. The residual silver amounts to 73·62 per cent. (Muspratt.)—The sulphurous acid is expelled from the salt by stronger acids, but not by acetic acid. (Berthier, *N. Ann. Chem. Phys.* 7, 82.)—The salt is insoluble in water, according to Berthier; very slightly, according to Muspratt; it scarcely dissolves in aqueous sulphurous acid, but easily in ammonia. (Berthier.) It dissolves in aqueous alkaline sulphites, forming double salts which easily decompose.

| | | | | | Muspratt. |
|---|---|---|---|---|---|
| $AgO$ | 116 | .... | 78·38 | .... | 79·02 to 77·76 |
| $SO^2$ | 32 | .... | 21·62 | .... | |
| $AgO,SO^2$ | 148 | .... | 100·00 | | |

F. Hyposulphate of Silver-oxide, or Silver-hyposulphate.—Formed by dissolving the carbonate of silver-oxide in aqueous hyposulphuric acid.—Crystalline system the right prismatic. *Fig.* 66, $a : a' =$

127°; $a : a$ backwards = 126°; $a : y$ = 153° 30′; $a$ : the face between $a$ and $t$ = 161° 36′; $a : u$ = 129° 35′; $u : m$ = 135° 26′; $u : t$ = 134° 34′.—The crystals are permanent in the air; blacken when exposed to light; and are resolved by heat into a grey powder, which, when dissolved in boiling water, leaves a small residue of sulphide of silver. Soluble in 2 parts of water at 16°. (Heeren.)

| | *Crystallized.* | | | | Heeren. |
|---|---|---|---|---|---|
| AgO | 116 | .... | 56·31 | .... | 56·15 |
| $S^2O^5$ | 72 | .... | 34·95 | | |
| 2HO | 18 | .... | 8·74 | | |
| $AgO,S^2O^5 + 2Aq.$ | 206 | .... | 100 00 | | |

G. Sulphate of Silver-oxide, or Silver-sulphate.—Formed by boiling silver-filings with 1½ pt. of oil of vitriol, the action being attended with evolution of sulphurous acid.—2. By dissolving the oxide or carbonate of silver in dilute sulphuric acid.—3. By mixing a solution of the nitrate with sulphuric acid, and evaporating to dryness.—4. By precipitating the nitrate with Glauber's salt, and washing the precipitate with a small quantity of cold water. The finest crystals of this salt are obtained from its solution in nitric acid. (Mitscherlich.) White crystals, belonging to the right prismatic system; very small, and shining; they contain no water. They are isomorphous with anhydrous sulphate and seleniate of soda, permanganate of baryta, and seleniate of silver-oxide. *Fig.* 59, $a : a'' = 136° 20'$; $a : a' = 125° 11'$. (Mitscherlich, *Pogg.* 12, 138; 25, 301.) Specific gravity 5·341. (Karsten.) It requires a very high temperature to decompose it, being then resolved, after previous fusion, into metallic silver, sulphurous acid, and free oxygen. (Gay-Lussac.) When mixed with charcoal, it is decomposed at a dull red-heat, yielding metallic silver, and a mixture of carbonic and sulphurous acid gases in equal volumes. (Gay-Lussac, *J. pr. Chem.* 11, 70.) Soluble in 87 parts of water, and in a smaller quantity of nitric acid. It dissolves more abundantly in oil of vitriol, and is partly precipitated from the solution on the addition of water. (Schnaubert. *Von der Verwandtschaft*, § 65.)

| | | | |
|---|---|---|---|
| AgO | 116 | ..... | 74·36 |
| $SO^3$ | 40 | ..... | 25·64 |
| $AgO,SO^3$ | 156 | ..... | 100·00 |

The following reaction of silver with sulphuric acid deserves more minute examination: Of a silver plate weighing 20 grains, and placed in a stoppered bottle with 2 drams of anhydrous sulphuric acid at ordinary temperatures, 6 grains dissolve without any evolution of sulphurous acid, and form a transparent brown liquid. The action of the anhydrous acid on the silver begins immediately, and the solution blackens the fingers, like other silver solutions. Fuming oil of vitriol likewise dissolves silver in the cold; and even common English oil of vitriol does the same, if previously concentrated by boiling. (A. Vogel, *Kastn. Arch.* 16, 108.)

H. Sulphocarbonate of Silver.—Aqueous sulphocarbonate of calcium mixed with nitrate of silver-oxide, forms a dark brown precipitate, which dissolves in excess of the calcium-salt, yielding a dark brown solution. The precipitate, after drying, is black, shining, and difficult to pulverize; and when distilled, gives off a large quantity of sulphur with a small quantity of sulphide of carbon, and leaves sulphide of silver mixed with charcoal. (Berzelius.)

I. Sulphide of Phosphorus and Silver.—*a. Hyposulphophosphite of Silver.—a. Bibasic.*—2AgS,PS. Formed by igniting *b* or *c*. Dark brown powder.—*β. Monobasic.* Silver reduced from the chloride by zinc and hydrochloric acid, then washed with hydrochloric acid and afterwards with water, and dried at the ordinary temperature, is moistened with protosulphide of phosphorus in the bulb-apparatus already described. (II, 213 and V, 26), and very gently heated in a stream of hydrogen gas. Combination takes place, attended with evolution of heat; and a sulphide of phosphorus containing a larger proportion of the latter element volatilizes; the rest of the excess of sulphide of phosphorus is removed by gentle heating in the current of hydrogen. If the silver is dried at a higher temperature, even at 60°, its greyish colour changes to silver-white, and it no longer combines so completely with the sulphide of phosphorus; so that spangles of silver remain mixed with the compound. Sulphide of silver previously prepared, likewise combines, but very imperfectly, with sulphide of phosphorus. The compound is black in mass, and yields a dark violet-brown powder. Heated to low redness in a retort, it changes to a pasty liquid, then gives off protosulphide of phosphorus with strong intumescence, and leaves a residue of sulphide of silver. (Berzelius, *Ann. Pharm.* 46, 254.)

| | | | | | Berzelius. |
|---|---|---|---|---|---|
| Ag | 108·0 | .... | 63·01 | .... | 63·76 |
| P | 31·4 | .... | 18·32 | .... | 18·00 |
| 2S | 32·0 | .... | 18·67 | .... | 18·25 |
| AgS,PS | 171·4 | .... | 100·00 | .... | 100·01 |

*b. Sulphophosphite of Silver.* When finely-divided silver is heated with sulphur and phosphorus in a current of hydrogen gas, combination takes place with the greatest violence, the greater part of the excess of phosphorus being volatilized: the rest must be driven off by heating the product in a stream of hydrogen. Grey mass, easily reduced by trituration to a light yellow powder, containing a few metallic spangles. Heated to commencing redness in a retort, it gives off sulphur, and leaves the dark brown compound I, *a*, *a*. Dissolves very readily in nitric acid, without separation of sulphur. (Berzelius.)

| | | | | | Berzelius. |
|---|---|---|---|---|---|
| 2Ag | 216·0 | .... | 65·98 | .... | 66·30 |
| P | 31·4 | .... | 9·59 | .... | 8·24 |
| 5S | 80·0 | .... | 24·43 | .... | 25·48 |
| $2AgS,PS^3$ | 327·4 | .... | 100·00 | .... | 100·02 |

*c. Sulphophosphate of Silver.* $2AgS,PS^5$. When the compound *a*, *β* (4AgS,PS) is gently heated with 4 atoms of sulphur, the whole melts; half of the resulting pentasulphide of phosphorus volatilizes; and, on cooling, there remains a brownish orange-yellow mass, which yields a deep yellow powder, and, when ignited out of contact of air, gives off sulphur, and is converted into 2AgS,PS. (Berzelius.)

## Silver and Selenium.

A. Protoselenide of Silver.—Found native in combination with a small quantity of selenide of lead. Silver fuses readily with selenium. It is blackened by selenium vapours, selenious acid, and seleniuretted hydrogen. The last-mentioned substance forms, with silver-nitrate, a

black precipitate, which becomes dark grey when dry, and when heated to redness, fuses without giving off selenium, and forms a silver-white, somewhat ductile globule. This compound does not part with the whole of its selenium when heated in the air for any length of time—not even when fused with borax, alkalis, or iron, which last, however, enters into combination with the selenide of silver, forming a dark grey, granular compound. Selenide of silver dissolves in boiling nitric acid, forming a solution of selenite of silver-oxide, which separates in the crystalline form on cooling, and in the pulverulent form when mixed with water. (Berzelius.)

*Native selenide of silver* occurs in thin plates with the cleavage-planes of the cube; its specific gravity is 8·00. It is harder than rock-salt, malleable, but less so than sulphide of silver; opaque, with a strong lustre; iron-black, and produces a streak of the same colour. When fused in a glass flask, it yields a scanty sublimate of selenium, and above that a sublimate of selenious acid. On charcoal, in the outer blowpipe flame, it fuses quietly; in the inner, with intumescence, and becomes red-hot again as it solidifies. Heated on charcoal with carbonate of soda, it yields a metallic globule, which, on cooling, becomes covered with a black film; but, on the addition of borax, is reduced to the state of pure silver, which remains bright. Dissolves very slowly in dilute nitric acid, but with tolerable facility in the fuming acid. (G. Rose, *Pogg.* 14, 471.)

| | *Artificial.* | | | Berzelius. | | *Native.* | | | G. Rose. |
|---|---|---|---|---|---|---|---|---|---|
| Ag..... | 108 | .... | 72·97 | .... 73·16 | 13Ag ... | 1404 | .... | 67·80 | .... 65·56 |
| Se..... | 40 | .... | 27·03 | .... 26·84 | Pb ..... | 104 | .... | 5·03 | .... 4·91 |
| | | | | | Fe ..... | | .... | | .... trace |
| | | | | | 14Se .... | 560 | .... | 27·08 | .... 25·93 |
| AgSe .... | 148 | .... | 100·00 | .... 100·00 | | 2068 | .... | 100·00 | .... 96·40 |

B. Biselenide of Silver.—To form this compound, selenide of silver precipitated by seleniuretted hydrogen is heated with excess of selenium, and the too great excess is removed by heating the product out of contact of air. Grey, somewhat malleable; fuses below a red-heat, forming a mass with specular surface. When ignited out of contact of air, it does not give off selenium; but if the air has access to it, half the selenium goes off, and the compound A remains.

*Calculation*, according to Berzelius.

| | | | |
|---|---|---|---|
| Ag ..... | 108 | .... | 57·49 |
| 2Se..... | 80 | .... | 42·51 |
| $AgSe^2$..... | 188 | .... | 100·00 |

C. Selenite of Silver-oxide, or Silver-selenite.—$AgO,SeO^2$.—Selenious acid added to nitrate of silver-oxide, throws down the monoselenite in the form of a white powder. The same salt crystallizes in needles from a nitric acid solution diluted with hot water. It is not blackened by light. Fuses almost as easily as horn-silver, forming a clear liquid, which, on cooling, solidifies in a white, opaque mass, friable, and having a crystalline fracture. When more strongly ignited, it gives off selenious acid and oxygen gas, and becomes covered with metallic silver. Dissolves very sparingly in cold water, somewhat more freely in hot water, and easily in nitric acid, from which it may be precipitated by cold water. (Berzelius.)

| | | | | | Berzelius. |
|---|---|---|---|---|---|
| AgO | 116 | .... | 67·44 | .... | 67·29 |
| $SeO^2$ | 56 | .... | 32·56 | .... | 32·71 |
| $AgO,SeO^2$ | 172 | .... | 100·00 | .... | 100·00 |

D. Seleniate of Silver-oxide, or Silver-selenrate.—Crystallizes in the same form as the sulphate. *Fig.* 59. $a : a'' = 135° 42'$; $a : a' = 123° 30'$. (Mitscherlich.)

## Silver and Iodine

A. Iodide of Silver.—Found native. Formed when silver and iodine are heated together; also as a precipitate, on mixing a dissolved silver-salt with hydriodic acid or an aqueous metallic iodide.—Pale yellow; turns brown on exposure to light, but less quickly than the chloride; fuses at a low red heat, forming a red liquid, which solidifies as a soft mass on cooling. (H. Davy.) The solidified mass is of a dirty yellow colour, opaque, and has a granular fracture. (Berzelius.) Sp. gr. 5·0262 (Karsten); 5·614 (Boullay). Assumes a deep yellow colour when heated. When paper is saturated with a solution of silver, and then with a dilute solution of iodide of potassium, the precipitated iodide of silver imparts to the paper a pale yellow colour, which becomes darker when heated, but resumes its original pale colour on cooling, even when touched with the cold finger. Any part of the paper moistened with potash turns white, and remains white when heated; similarly with ammonia, excepting that the latter gradually evaporates, and consequently the dark colour is produced on the application of heat. (Talbot, *Phil. Mag. J.* 12, 258; also *Pogg.* 46, 326.) The experiment may be better made upon porcelain, inasmuch as the paper easily burns away. (Erdmann, *J. pr. Chem.* 14, 123.)—Volatilizes before the blowpipe, producing a green flame, and a white, penetrating smoke, and leaving only a small quantity of silver on the charcoal. Fused with hydrate of potash, it yields metallic silver, iodide of potassium, and oxygen gas. (H. Davy.)—Zinc and iron, when water is present, separate metallic silver from the iodide; antimony and bismuth have no action upon it, even on boiling; aqueous potash or soda gives it a brownish colour, and decomposes it imperfectly; carbonate of potash or soda alters its colour, but slightly, and the carbonates of baryta, strontia, and lime, as well as pure strontia, lime, and baryta do not act upon it in the humid way. Iodide of silver, exposed to a current of chlorine gas at ordinary temperatures, turns white, takes up chlorine, and then, on the application of a gentle heat, gives off its iodine. In this reaction, 234 pts. (1 At.) of iodide of silver yield from 142·5 to 143·3 and 145·5 of chloride. (Berzelius, *Pogg.* 14, 558.)—Strong nitric or sulphuric acid expels iodine from it, and converts it into nitrate or sulphate of silver-oxide; on the addition of water, part of the iodine is restored to its place.—Dilute sulphuric acid has no action on iodide of silver; neither has phosphoric acid. (Brandes, *Schw.* 61, 255.) A solution of mercuric nitrate dissolves iodide of silver. (Preuss.)—Aqueous ammonia causes iodide of silver to assume a paler colour, and, according to H. Rose (*Pogg.* 31, 583), dissolves a trace of it. 1 part of iodide of silver dissolves in 2510 parts of aqueous ammonia of specific gravity 0·96. (Martini, *Schw.* 56, 154.) Water does not dissolve iodide of silver; concentrated solutions of the chlorides of potassium and sodium dissolve it in considerable quantity.

| | | | |
|---|---|---|---|
| Ag | 108 | .... | 46·15 |
| I | 126 | .... | 53·85 |
| AgI | 234 | .... | 100·00 |

The *native iodide of silver* from Mexico is malleable, translucent, and of a pearly grey colour. (Noggeräth, *Schw.* 51, 363.)—Before the blowpipe, it fuses very easily, turns red, and colours the flame violet. (Del Rio, *Schw.* 50, 494.) *Comp.* Vauquelin (*Ann. Chim. Phys.* 29, 59; also *Schw.* 45, 26).

B. Iodate of Silver-oxide, or Silver-iodate.—Formed by precipitating a solution of silver-nitrate with iodic acid (Gay-Lussac), or iodate of soda (Rammelsberg).—White precipitate. (Gay-Lussac.) Crystallizes from the ammoniacal solution in small, brilliant, rectangular prisms, free from ammonia. (Rammelsberg, *Pogg.* 44, 572.)—Decomposed by heat into oxygen gas and iodide of silver. (Benckiser, Rammelsberg.) Hydrochloric acid decomposes it, forming chloride of silver, terchloride of iodine, water, and chlorine gas (Filhol):

$$AgO,IO^5 + 6HCl = AgCl + ICl^3 + 6HO + 2Cl.$$

Dissolves in ammonia, forming a liquid from which sulphurous acid precipitates iodide of silver. (Gay-Lussac, *Gilb.* 49, 255.) Sparingly soluble in nitric acid. (Benckiser, *Ann. Pharm.* 17, 255.)

| | | | | Benckiser. |
|---|---|---|---|---|
| AgO | 116 | .... 41·13 | .... | 40·57 |
| $IO^5$ | 166 | .... 58·87 | .... | 59·43 |
| $AgO,IO^5$ | 282 | .... 100·00 | .... | 100·00 |

Or:

| | | | | Benckiser. | Rammelsberg. |
|---|---|---|---|---|---|
| AgI | 234 | .... 82·98 | .... | 82·17 | .... 83·84 |
| 6O | 48 | .... 17·02 | .... | 17·83 | .... 16·16 |
| | 282 | .... 100·00 | .... | 100·00 | .... 100·00 |

C. Periodate of Silver-oxide, or Silver-periodate.—*a. Bibasic.*—*a. Mono-hydrated.*—On treating the ter-hydrated salt with warm water, which does not dissolve any of it, this compound remains in the form of a dark, red-brown mass, which yields a red powder, and, when ignited, is resolved into 17·25 per cent. of oxygen gas. 1·95 of water, and 80·44 of a mixture of silver and iodide of silver.—*β. Ter-hydrated.*—Formed by mixing nitrate of silver-oxide with a solution of bibasic periodate of soda in dilute nitric acid, washing the pale green precipitate with water acidulated with nitric acid, and dissolving it in warm, dilute nitric acid, from which the salt separates in shining, straw-yellow crystals on cooling. When heated, it is resolved into 16·66 per cent. of oxygen gas, 6·17 of water, and 77·30 of a mixture of iodide of silver and metallic silver. Both *α* and *β* dissolve in warm nitric acid. On leaving the solution to cool, the yellow salt *β* separates out; but if the solution be evaporated, the nitric acid withdraws half the oxide of silver, and allows the monobasic salt to crystallize out. (Ammermüller & Magnus.)

| | | | | Ammermüller & Magnus. | | | | | Ammermüller & Magnus. |
|---|---|---|---|---|---|---|---|---|---|
| 2AgO | 232 | .... | 54·85 | | 2AgO | 252 | .... | 52·61 | .... |
| $IO^7$ | 182 | .... | 43·02 | | $IO^7$ | 182 | .... | 41·27 | .... |
| HO | 9 | .... | 2·13 | .... 1·95 | 3HO | 27 | .... | 6·12 | .... 6·17 |
| $2AgO,IO^7 + Aq.$ | 423 | .... | 100·00 | .... | +3Aq. | 441 | .... | 100·00 | |

*b. Monobasic.* Formed when the solution of the salt *a*, *β* in warm nitric acid is evaporated with the aid of heat. The salt then separates, even before cooling, in orange-yellow, anhydrous crystals, which are resolved by heat into oxygen gas and iodide of silver. When immersed in cold water, which takes up half the acid without any of the oxide of silver, they fall to pieces and produce a straw-yellow powder, consisting of the ter-hydrated bibasic salt; in warm water they are converted into the red mono-hydrated salt *a*, *a*. Both the monobasic and the bibasic salt, when boiled with water or nitric acid, yield traces of iodate of silver-oxide, easily recognized by its white colour and sparing solubility. (Ammermüller & Magnus, *Pogg.* 28, 516.)

| | | | Or: | | | Ammermüller & Magnus. |
|---|---|---|---|---|---|---|
| AgO | 116 | 38·92 | AgI | 234 | 78·52 | 78·58 |
| $IO^7$ | 182 | 61·08 | 8O | 64 | 21·48 | 21·25 |
| $AgO,IO^7$ | 298 | 100·00 | | 298 | 100·00 | 99·83 |

## Silver and Bromine.

A. Bromide of Silver.—Found native.—1. A solution of silver-nitrate mixed with aqueous hydrobromic acid or bromide of potassium, yields a yellowish white precipitate. (Balard.) The same precipitate is formed by bromine. On adding a silver-solution in small successive portions to an aqueous mixture of hydrobromic and hydrochloric acids, bromide of silver is first precipitated, which assumes a pure grey colour on exposure to light—the chloride, which is coloured violet by the action of light, not being precipitated till afterwards. (Berthier, *Ann. Chim. Phys.* 77, 417.)

The precipitate dried in the shade is yellow (Balard), of specific gravity 6·3534 (Karsten), and when heated, fuses into a reddish liquid, which, on cooling, solidifies in a yellow, translucent, horny mass. (Balard.) Crystallizes in octohedrons from its solution in aqueous hydrobromic acid. (Löwig.)

| | | | Balard. | Löwig. |
|---|---|---|---|---|
| Ag | 108·0 | 57·94 | 58·9 | 58·95 |
| Br | 78·4 | 42·06 | 41·1 | 41·05 |
| AgBr | 186·4 | 100·00 | 100·0 | 100·00 |

The precipitate blackens if exposed to light while moist, but not so quickly as the chloride. (Balard.) The action of light does not turn it violet, like the chloride, but pure grey. (Berthier.)—Bromide of silver, strongly ignited with carbonate of soda, yields silver and bromide of sodium; but at a lower temperature, it fuses with the carbonate of soda into a turbid mass, from which the carbonate of soda may be dissolved out by water in its original state. (Berzelius, *Lehrb.*) With zinc and dilute sulphuric acid, it yields metallic silver. (Balard.) When heated in a stream of chlorine gas, it is converted into chloride of silver, but much less quickly than the iodide. (Berzelius, *Pogg.* 14, 565.) When diffused through water, it is immediately decomposed by chlorine. (Berthier.)—Aqueous hypochlorous acid converts it into chloride of silver and bromate of silver-oxide, with evolution of bromine and chlorine. (Balard.)—Boiling oil of vitriol separates a small quantity of bromine vapour from bromide of silver; boiling nitric acid has no action upon it. (Balard.)—Solution of mercuric nitrate takes up bromide of silver.

(Wackenroder.)—Bromide of silver dissolves in strong hydrobromic acid and in strong hydrochloric acid. (Löwig.)—It is scarcely soluble in dilute ammonia, but easily in strong ammonia.—It is likewise slightly soluble in a concentrated solution of bromide of potassium or bromide of sodium. (Löwig.)—It dissolves in a hot solution of sal-ammoniac, very sparingly in aqueous carbonate, sulphate, or succinate of ammonia, least of all in nitrate of ammonia. (Wittstein.)

*Native Bromide of Silver.* The variety from Plateros in Mexico, mixed with a large quantity of arseniate and carbonate of lead, is of a yellowish olive-green colour, of specific gravity 5·8 to 6·02, and crystallized in cubes and octohedrons. Its light green powder turns grey when exposed to light.—The ore from Chanaveillo in Chili is a mixture of bromide and chloride of silver, associated with other minerals. (Berthier, *Ann. Chim. Phys.* 77, 417; 79, 164.)

B. Aqueous Bromide of Silver and Hydrogen, or Acid Hydrobromate of Silver oxide.—1 At. concentrated hydrobromic acid dissolves nearly 1 At. bromide of silver, which crystallizes out on cooling, and is precipitated by dilution with water. (Löwig.)

C. Hypobromite of Silver-oxide.—Oxide of silver immersed in bromine-water yields bromide of silver and aqueous hypobromite of silver-oxide, which is easily resolved into bromide of silver and bromate of silver-oxide. (Balard.)

D. Bromate of Silver-oxide, or Silver-bromate.—Free bromic acid and bromate of potash added to solution of silver-nitrate, throw down a white powder, which blackens very slightly on exposure to light. (Balard.) According to Rammelsberg, it soon turns grey when exposed to light. Froths up when heated, and is resolved into oxygen gas and bromide of silver (Löwig); if the heat be suddenly applied, the decomposition is attended with fiery detonation, volatilization of part of the bromide of silver in the form of a yellow vapour, and evolution of a faint odour of bromine. (Rammelsberg, *Pogg.* 52, 94.) Detonates on red-hot coals like nitre. (Löwig.) Converted into chloride of silver by digestion in hydrochloric acid. (Rammelsberg.) Insoluble in water and nitric acid; soluble in ammonia. (Löwig.) Slightly soluble in water. (Rammelsberg.)

| | | | | | Rammelsberg. |
|---|---|---|---|---|---|
| $AgO$ ..... | 116·0 | .... | 49·49 | .... | 49·73 |
| $BrO^5$ ..... | 118·4 | .... | 50·51 | .... | 50·27 |
| $AgO,BrO^5$ .... | 234·4 | .... | 100·00 | .... | 100·00 |

## Silver and Chlorine.

A. *Dichloride of Silver?—Black Chloride of Silver.—Formation.* 1. White chloride of silver obtained by precipitation, and exposed to light, where moisture is present, gives off chlorine, and assumes first a violet, then a brownish grey colour, and finally becomes black.—When the white chloride of silver is immersed in water in a stoppered bottle, and exposed to sunlight, a strong odour of chlorine is observed after 24 hours; if the chlorine be allowed to evaporate from the water, a fresh quantity is disengaged by the continued action of the light. The evolution of

chlorine from chloride of silver thus exposed to light goes on for several months, becoming, however, continually weaker; and at last, instead of chlorine, the water is found to contain hydrochloric acid, which has been formed from the chlorine (with evolution of oxygen). The innermost parts of the chloride of silver remain, however, unaltered. (Wetzlar, *Schw.* 52, 406.) Thénard and Fischer likewise observed this evolution of chlorine. According to Scheele and Bucholz, the blackening is attended with evolution of hydrochloric acid; the same is stated by Berthollet (*Stat. chim.* 1, 195); and moreover, that the formation of the hydrochloric acid is not attended with evolution of oxygen. The blackening by exposure to light does not take place unless moisture is present; hence it is not produced in vacuo over oil of vitriol. Covering the white chloride with alcohol likewise protects it from blackening for a considerable time. (Seebeck, *Pogg.* 9, 172.) The blackening takes place less quickly under water containing chloride of potassium or chloride of sodium in solution, than under pure water. (Wetzlar.) White chloride of silver does not blacken by exposure to light if immersed in nitric acid. (Scheele.) According to Wetzlar, it blackens under nitric or hydrochloric acid, but not under chlorine-water or solution of ferric sulphate. In nitric acid of specific gravity 1·23, it assumes a pale violet colour in two days, and becomes dark violet in sunshine in the course of an hour. In nitric acid of specific gravity 1·4, it remains white in daylight, but on exposure to direct sunshine for an hour, it acquires a very pale violet tint, which does not increase in four hours. (Wittstein, *Repert.* 63, 220.) When a silver-solution mixed with sulphate or acetate of ferric oxide is precipitated by common salt, the precipitate does not blacken when exposed to light for two hours, but acquires a certain amount of grey colouring in a few days. (A. Vogel, *J. pr. Chem.* 20, 365.) If the precipitated chloride of silver contains a trace of calomel, it does not blacken on exposure to light. (H. Rose.)—2. Silver immersed in an aqueous solution of sesquichloride of iron, protochloride of copper, or protochloride of mercury, takes up—provided the immersion be not too long continued—only as much chlorine as is required to form the black chloride of silver, the action being likewise attended with the formation of protochloride of iron, dichloride of copper, or dichloride of mercury.—The solution of either of these three metallic chlorides immediately forms a black spot upon silver. On this reaction is grounded Smithson's process for recognizing an aqueous metallic chloride, viz., by its property of blackening a bright silver surface on the addition of ferric or cupric sulphate. A silver spoon acquires a black tarnish on being moistened with solution of sal-ammoniac, only when it contains copper, or when a piece of copper is immersed in the liquid. (Wetzlar.) In opposition to these statements, Schaffhäutl (*Ann. Pharm.* 44, 27) maintains that finely divided silver has no action on sesquichloride of iron.—To obtain the black chloride of silver in the greatest possible state of purity by the process just described, silver-leaf is immersed in an aqueous solution of sesquichloride of iron or protochloride of copper. It immediately separates into little spangles, and is subsequently converted into a brownish black powder, which must be washed. Pulverulent silver precipitated by green vitriol is not so well adapted to the purpose, because it cakes together; hence it requires to be left for a longer time in contact with the iron or copper solution, and is thereby partly transformed into white chloride of silver, which forms a brown mixture with the black chloride. (Wetzlar.)—A. Vogel obtained with silver-leaf and a solution of corrosive sublimate, a *white* pulverulent

mixture of chloride of silver and calomel.—3. The black chloride of silver may be formed from the suboxide and its salts by the action of hydrochloric acid. (Wohler, *Ann. Pharm.* 30, 3.)—Suboxide of silver precipitated from the citrate by potash yields a brown substance when treated with hydrochloric acid.—An aqueous solution of citrate of suboxide of silver forms the same precipitate with hydrochloric acid. (Wöhler.)

The subchloride prepared by (1) and (2) is black; by (3) brown; and assumes the metallic lustre under the burnishing steel. (Wöhler.)

The compound (3) heated to the melting point of protochloride of silver, cakes together, and is converted into a yellow mixture of metallic silver and the protochloride. (Wöhler.) Aqueous ammonia extracts protochloride of silver from the subchloride (whether prepared by 1, 2, or 3), and leaves a black powder consisting of metallic silver, soluble with effervescence in nitric acid. (Scheele, Wetzlar, Dulk, Wöhler.) Strong boiling hydrochloric acid, or a boiling solution of common salt acts in a similar manner to ammonia. (Wetzlar.) According to Berthollet, black chloride of silver is perfectly soluble in ammonia. Subchloride of silver retains its black colour when immersed in nitric acid (A. Vogel, *Gilb.* 72, 286); even the hot concentrated acid does not extract silver from it—a proof that it does not contain any free metal. (Wetzlar.) Hot nitric acid takes up a portion of the silver from (2), and leaves a brownish red residue, almost wholly soluble in ammonia. (Dale, *J. pr. Chem.* 3, 232.) Subchloride of silver prepared by (1) or (2), is converted by immersion in chlorine-water, sesquichloride of iron, or protochloride of copper, into white chloride of silver, the action being attended with formation of protochloride of iron or dichloride of copper. (Wetzlar.)

B. Protochloride of Silver.—*Horn-silver*, *Luna-cornea.*—Found native as *Horn-silver.*—*Formation.* 1. Silver immersed in chlorine gas or chlorine water, is slowly converted into horn-silver, without, however, exhibiting visible combustion in the gas.—2. Hydrochloric acid gas (even when perfectly dry) passed over red-hot silver, yields hydrogen gas and chloride of silver; on the other hand, chloride of silver heated to redness in an atmosphere of hydrogen, yields hydrochloric acid gas and metallic silver. (Boussingault, *Ann. Chim. Phys.* 54, 260; also *J. pr. Chem.* 2, 155.) The conversion of the silver into chloride is only superficial, because the chloride first formed protects the inner portions of the metal. If the silver is enveloped in alumina, into which the fused chloride can penetrate, a larger portion of the metal becomes converted into chloride; and if the alumina is mixed with common salt, which forms an easily fusible compound with chloride of silver, the metallic silver is completely converted into chloride. If hydrochloric acid gas be passed into a muffle, under which silver is fusing, the quantity of the metal gradually diminishes, because chloride of silver is formed and evaporates. When, therefore, silver is heated to redness in a mixture of brick-dust and common salt, and the crucible is sufficiently porous to admit the ingress of the aqueous vapour generated by the combustion of the fuel, the common salt is decomposed by the silica, yielding silicate of soda and hydrochloric acid, (II. 353), and the latter converts the silver into chloride, which then fuses with the rest of the chloride of sodium. On this reaction is grounded the American method of separating silver from gold by cementation. (Vid. *Gold.*) Silica acts like brick-dust, but less efficiently, because the mass becomes more vitrefied. Silver heated to redness with brick-dust and common salt in a porcelain tube, remains unaltered, even when a current

of dry air is passed through the tube. Silver is not altered by ignition with common salt under the muffle, even for three hours. (Boussingault.)—3. Silver immersed in aqueous hydrochloric acid is superficially converted into chloride, with evolution of hydrogen, and a small portion of the chloride dissolves. (Proust.) If the air has access to the liquid, silver dissolves in the course of a week in hydrochloric acid of specific gravity 1·2, forming a solution, from which water throws down chloride of silver. (Fischer, *Schw.* 51, 193.) In this case, the oxygen of the air combines with the hydrogen of the acid. The conversion of the silver into chloride likewise takes place with facility, when the hydrochloric acid contains substances which readily give up their oxygen, such as arsenic acid or peroxide of manganese. (Scheele, *Opusc.* 1, 169.) The same effect is produced by the addition of blue vitriol or protochloride of copper to the hydrochloric acid. (Sonneschmidt, Karsten.) Silver leaf, or silver powder, immersed in a solution of common salt, to which the air has access, is converted—with simultaneous formation of soda, by the action of atmospheric oxygen—into chloride of silver, which then dissolves in the solution of common salt. (Wetzlar, *Schw.* 52, 473.) Piastres from a sunken Spanish ship, raised from the water after the lapse of many years, were found to be converted into chloride of silver. (Proust.)—4. Finely divided silver immersed in hypochlorous acid gas, aqueous hypochlorous acid, or its salts, is converted into chloride, with evolution of oxygen. (Balard.)—5. Oxide of silver and hydrochloric acid yield water and chloride of silver. Oxide of silver boiled in an aqueous solution of chloride of potassium or chloride of sodium, forms chloride of silver and an aqueous solution of the alkali, containing only a trace of chloride and oxide of silver. (Wetzlar, *Schw.* 53, 100.)—6. All salts of silver-oxide, even those which are insoluble in water, such as the carbonate, phosphate, chromate, and oxalate, are converted by aqueous hydrochloric acid, or by aqueous metallic chlorides, into chloride of silver.—7. Chlorine likewise precipitates chloride of silver from solutions of that metal, generally, however, with simultaneous formation of hypochlorite of silver-oxide, which is soon resolved into chloride and chlorate.—8. Sulphide of silver, heated in chlorine gas, is slowly converted into chloride. In this reaction, 124 pts. (1 At.) of sulphide of silver yield from 143·2 to 144·2 pts. of chloride. (Berzelius.) Sulphide of silver, roasted with common salt, yields chloride of silver and sulphate of soda. With aqueous protochloride of copper, mixed with common salt, it forms chloride of silver and dichloride of copper, which remains dissolved in the common salt, &c. (p. 152.)—9. Heated iodide, or bromide of silver, is converted by chlorine gas (the bromide very slowly) into chloride of silver. 234 pts. (1 At.) of iodide of silver yield from 142·5 to 143·2 and 145·5 pts. of chloride. (Berzelius, *Pogg.* 14, 558.)

*Preparation.* By precipitating nitrate of silver-oxide with hydrochloric acid or common salt, and washing and drying the precipitate, which must be excluded from light during the whole series of operations.

*Properties.* The native chloride crystallizes in the forms shown in *figures* 1, 2, 3, 4, and 5. It is malleable and flexible, of specific gravity 5·55, greyish white, with an unctuous adamantine lustre, and translucent. Horn-silver likewise crystallizes in octohedrons from a solution in aqueous ammonia or hydrochloric acid; when thrown down from a dissolved silver-salt by hydrochloric acid, it forms a white, curdy precipitate. When

cooled from a state of fusion, it solidifies, with considerable expansion (Persoz, *Chim. Molecal.* 242), in a colourless, transparent, strongly refracting, horny mass, which takes impressions from the nail. Before fusion, its specific gravity is 5·501 (after blackening in the sun, 5·5671). (Karsten.) After fusion and solidification, 5·4548 (Proust); 5·4582 (Karsten); 5·548 (P. Boullay). Fuses at 260°, previously assuming a yellowish colour, and forms an orange-yellow, transparent liquid, which sinks into the pores of an earthen crucible, and volatilizes without decomposition at higher temperatures.

| | | Ure. | Marignac. |
|---|---|---|---|
| Ag | 108·0 .... 75·314 .... | 75·524 .... | 75·34 |
| Cl | 35·4 .... 24·686 .... | 24·476 .... | 24·66 |
| AgCl | 143·4 .... 100·000 .... | 100·000 .... | 100·00 |

| | Berzelius. *earlier.* | Berzelius. *later.* | Wenzel. | Val. Rose. | Bergman Bucholz. |
|---|---|---|---|---|---|
| Ag | 75·24 .... | 75·33 .... | 75·33 .... | 75·18 .... | 75 |
| Cl | 24·66 .... | 24·67 .... | 24·67 .... | 24·82 .... | 25 |
| AgCl | 100·00 .... | 100·00 .... | 100·00 .... | 100·00 .... | 100 |

| Or: | Berzelius. | Marcet. | Proust. | Val. Rose. | Zaboada. |
|---|---|---|---|---|---|
| AgO | 80·903 .... | 80·95 .... | 82 .... | 82·26 .... | 82·3 |
| Cl—O | 19·097 .... | 19·05 .... | 18 .... | 16·74 .... | 17·7 |
| | 100·000 .... | 100·00 .... | 100 .... | 100·00 .... | 100·0 |

| | Bucholz. | Chenevix. | Kirwan. |
|---|---|---|---|
| AgO | 82·5 .... | 83 .... | 83·46 |
| Cl—O | 17·5 .... | 17 .... | 16·54 |
| | 100·0 .... | 100 .... | 100·00 |

*Decompositions.* White horn-silver turns violet and black on exposure to light. (*Comp.* III, 616.)—2. Heated on charcoal before the blowpipe, it yields metallic silver, with evolution of an odour of hydrochloric acid. On the addition of oxide of copper, the flame becomes blue. ¶ Wittstein recommends, for the reduction of chloride of silver, to mix 2 parts of it intimately with 1 part of charcoal; he is of opinion that the reduction is due to the hydrogen in the charcoal. (*Repert. Pharm.* 3rd ser. 2, 1.) ¶—3. When heated in an atmosphere of carbonic oxide gas, it is rapidly decomposed, yielding phosgene gas and metallic silver. (Göbel, *J. pr. Chem.* 6, 388.)

$$AgCl + CO = Ag + COCl.$$

It is not decomposed by ignition with pure charcoal.—4. Heated with phosphorus, it yields chloride of phosphorus and metallic silver, with which a considerable quantity of chlorine remains mixed. (H. Rose, *Pogg.* 27, 117.) When gently heated in phosphuretted hydrogen gas, it is very easily decomposed into hydrochloric acid, phosphorus, and silver. (H. Rose, *Pogg.* 24, 334.)—5. When boiled in the freshly-precipitated state with aqueous alkaline sulphates, it is reduced somewhat rapidly to the metallic state; but the resulting metal, if required pure, must be washed with ammonia. (Berthier, *N. Ann. Chim. Phys.* 7, 82.) Cold aqueous sulphurous acid has no effect upon chloride of silver; but the same liquid, when hot, colours it light grey. (A. Vogel.)—6. Arsenic, antimony, bismuth, zinc, cadmium, tin, lead, iron, copper, and mercury, agitated with chloride of silver and water, separate the silver with evolution of heat,

the action being greatly facilitated by the presence of free hydrochloric acid, and by the action of heat. Zinc and iron act without the addition of water, provided only that the surrounding atmosphere contains moisture; but in vacuo, or under alcohol or ether, the decomposition does not take place. With the other metals, the presence of water is necessary; of these, cadmium, lead, and arsenic, act the most rapidly; antimony, copper, and mercury, act slowly; tin and bismuth most slowly of all. (Fisher, *Gilb.* 42, 230; 72, 300; *Pogg.* 6, 43.) Zinc and iron are the only metals which decompose chloride of silver under water at ordinary temperatures. Tin, lead, copper, bismuth, and antimony decompose it only in presence of mercury, which takes up the silver, or in presence of free hydrochloric acid. (Karsten.)—For the decomposition of horn-silver by mercury, the presence of common salt is necessary. (Sonnenschmidt, *Ann. Chim. Phys.* 51, 349.)—7. By heating with cinnabar, sulphide of silver and protochloride of mercury are obtained. (Wenzel, *Verwandtsch.* 452.)—Aqueous solution of green vitriol exerts no decomposing action. (Keir, *Schw*, 53, 166; Wetzlar, *Schw.* 51, 373.)—8. Chloride of silver, fused with hydrate of potash or soda, with carbonate of potash or soda, or with lime, yields metallic silver and a chloride of the alkali-metal, with evolution of oxygen gas and water.—Aqueous solution of potash, of specific gravity not less than 1·25, decomposes recently precipitated and still moist chloride of silver rapidly and completely, yielding aqueous chloride of potassiu a nd pure oxide of silver, which, after washing, is completely soluble in nitric acid. Cold or dilute potash-ley has no action on chloride of silver; and if the chloride has once been dried, it is but incompletely decomposed, even by long boiling with strong potash-ley. (Gregory, *Phil. Mag. J.* 22, 284; *comp.* Wetzler, *Schw.* 53, 99.)—Aqueous carbonate of potash decomposes chloride of silver. (Thomson.) The chloride of silver blackens when boiled with carbonate of potash, apparently from formation of dichloride of silver.—9. Cold oil of vitriol does not decompose chloride of silver; boiling oil of vitriol decomposes it slowly, with evolution of hydrochloric acid and formation of sulphate of silver-oxide; part of the horn-silver likewise dissolves, without decomposition, in hot oil of vitriol, and does not separate again on cooling. (A. Vogel.)

Chloride of silver dissolves sparingly in concentrated hydrobromic acid (Löwig);—in concentrated hydrochloric acid; also sparingly in hot alcohol mixed with hydrochloric acid, and partly separates again on cooling (Erdmann, *J. pr. Chem.* 19, 341); it dissolves in sal-ammoniac solution; easily, according to Brett; with difficulty, according to Wittstein, but not in other ammoniacal salts;—sparingly in a strong solution of chloride of potassium, chloride of sodium, and a few other metallic chlorides;—copiously in aqueous alkaline hyposulphites (forming a chloride of the alkali-metal, and hyposulphite of silver-oxide and the alkali: *Herschel*);—abundantly in ammonia even when very dilute (vid. *Ammonio-chloride of silver*);—it likewise dissolves in aqueous mercuric nitrate, and is easily precipitated therefrom by hydrochloric acid, sal-ammoniac, or common salt; imperfectly by nitrate of silver-oxide, and not at all by nitric acid. (Wackenroder, *Ann. Pharm.* 41, 317.) In other liquids, chloride of silver is insoluble.—Chloride of silver in the melted state is capable of absorbing a very small quantity of chlorine gas, which easily escapes again on cooling. (Berzelius.)—It does not absorb the vapour of anhydrous sulphuric acid. (H. Rose.)

*Powder for the cold Silvering of Copper and Brass: a.* 1 part of precipitated chloride of silver, 2 of alum, 8 of common salt, and 8 of

tartar.—*b.* 1 pt. of chloride of silver, 1 of prepared chalk, somewhat more than 1 of common salt, and 3 of pearl-ash.—*c.* 1 part of silver precipitated by copper, 4 of common salt, 4 of sal-ammoniac, and $\frac{1}{4}$ of corrosive sublimate; the whole made up into a paste with water.—The surface of the metal to be silvered is cleansed by boiling with water, alum, and tartar, then heating it to redness and polishing, or by friction with tripoli; it is then moistened with solution of common salt, and some of the powder is rubbed into it, after which it is washed and dried with a soft woollen cloth.

C. Aqueous Chloride of Silver and Hydrogen, or Acid Hydrochlorate of Silver-oxide.—Chloride of silver dissolves somewhat copiously in strong hydrochloric acid. The same solution is formed by the action of strong hydrochloric acid on metallic silver, with free access of air (p. 163, 3). The solution when evaporated, yields octohedrons of chloride of silver: it is almost completely precipitated by water, the liquid exhibiting a milky turbidity.—Tolerably dilute hydrochloric acid is likewise capable of dissolving a certain quantity of silver; a solution of 1 pt. of silver-nitrate in 15,000 of water, becomes turbid on the addition of a small quantity of hydrochloric acid, and clear again on the addition of a further quantity; it still, however, yields a precipitate with sulphuretted hydrogen, even when 7,500 parts of hydrochloric acid have been added. (Reinsch, *J. pr. Chem.* 13, 133.)

D. Hypochlorite of Silver-oxide, or Silver-hypochlorite.—When oxide of silver is diffused in water and agitated while a stream of chlorine is passed through the liquid, heat is evolved, and chloride and peroxide of silver are formed, together with a liquid of strong bleaching power, which becomes turbid in a few seconds, depositing chloride of silver, and being converted into a solution of chlorate of silver-oxide, which no longer possesses bleaching power. If the passage of chlorine through the bleaching liquid be continued, chloride of silver is formed, while hypochlorous and chloric acids remain in solution. An alkali added to the bleaching liquid, liberates oxygen gas, and precipitates a mixture of chloride and peroxide of silver.—A similar action is exerted by chlorine on the aqueous solution of chlorate, nitrate, or acetate of silver-oxide, the acid of the silver-salt being set free. (Balard, *Ann. Chim. Phys.* 57, 241.)

E. Chlorite of Silver-oxide, or Silver-chlorite.—Formed by precipitating a solution of silver-nitrate with an alkaline chlorite containing a slight excess of alkali, boiling the precipitate with water, filtering hot, and cooling to the crystallizing point. If but a trace of free chlorous acid were present at the precipitation, it would cause the product to resolve itself into chloride of silver and chlorate of silver-oxide:

$$3(AgO,ClO^3) = AgCl + 2(AgO,ClO^5).$$

Yellow crystalline scales. The dried salt detonates even when heated to 105°, or by contact with strong hydrochloric acid. With dilute hydrochloric acid, it yields 81·53 per cent. of chloride of silver. It sets fire to sulphur when mixed with that substance by means of a glass rod. It is not decomposed by boiling under water. (Millon, *N. Ann. Chim. Phys.* 7, 329.)

| | *Crystallized.* | | Millon. |
|---|---|---|---|
| AgO..... | 116·0 .... | 66·13 .... | 65·66 |
| $ClO^3$..... | 59·4 .... | 33·87 .... | |
| $AgO,ClO^3$ ..... | 175·4 .... | 100·00 | |

F. Chlorate of Silver-oxide, or Silver-chlorate.—1. Formed by passing chlorine gas through water in which silver-oxide is diffused, till bubbles of oxygen are evolved, then filtering from the chloride of silver, and evaporating to the crystallizing point. (Chenevix.) The filtrate at first contains hypochlorite of silver-oxide. (*vid. sup.*)—2. By dissolving silver-oxide in aqueous chloric acid, the action being accompanied with evolution of heat. (Vauquelin, *Ann. Chim.* 95, 124.)—White, opaque, four-sided prisms with oblique terminal faces, having the taste of nitrate of silver-oxide. (Vauquelin.)—The salt, when slightly heated, gives off oxygen with effervescence, and is reduced to chloride of silver. (Chenevix.) When mixed with sulphur, it detonates with the utmost violence on the slightest pressure. (Chenevix.) Thrown on red-hot coals, it detonates with a vivid light, and is converted into chloride. (Vauquelin.) Hydrochloric, nitric, and acetic acid resolve it into chloride of silver and oxygen gas which escapes. (Chenevix.) Chlorine, passed through the solution of this salt, causes an evolution of oxygen, and throws down chloride of silver, while chlorate of silver-oxide remains in solution.—The salt dissolves in from 10 to 12 parts of cold water (Vauquelin); in 8 to 10 pts. of cold, and 2 parts of warm water, and is slightly soluble in alcohol. (Chenevix.)

G. Perchlorate of Silver-oxide, or Silver-perchlorate.—The solution of silver-oxide in the aqueous acid yields no crystals when evaporated in the hot-air chamber, but a white powder. This powder fuses when somewhat strongly heated, forming but a small quantity of chloride of silver, and, on cooling, solidifies in the crystalline form. At a temperature somewhat below redness, it is suddenly decomposed. Its aqueous solution turns brown when exposed to light; paper saturated with it and then dried, detonates violently at 200°. It deliquesces in the air, and dissolves in strong alcohol. (Serullas, *Ann. Chim. Phys.* 46, 307.)

H. Chloriodide of Silver.—See page 157.

¶ I. Chlorobromide of Silver.—Found native in Chili.—A specimen imported by Vice-Admiral Sir George Seymour, and analysed by Col. Yorke (*Chem. Soc. Qu. J.* 4, 149), presented the appearance of a waxy, sectile substance, diffused in veins through and partially coating a red ochreous matrix containing portions of quartz: the whole specimen weighed about 60 lbs. The sectile substance, when cleared from ochre, was nearly black externally, but internally of a greenish yellow colour, translucent, and crystalline. The veins varied in thickness from $\frac{1}{4}$ of an inch to microscopic minuteness. The ochreous matter contained occasionally very small cubic crystals disseminated in it, and the coating was in some parts marked by impressions indicating some of the more complicated modifications of the cube. Sp. gr. of the chlorobromide 5·53 (Yorke), 0·702 (Dufrénoy).

| | | | | | Yorke. |
|---|---|---|---|---|---|
| 2AgBr | 372·8 | .... | 46·42 | .... | 46·8 |
| 3AgCl | 430·2 | .... | 53·58 | .... | 53·2 |
| 2AgBr + 3AgCl | 803·0 | .... | 100·00 | .... | 100·0 |

For other analyses of chlorobromide of silver, *vid.* Domeyko, *Ann. Min.* [4],6, 153. ¶

## Silver and Fluorine.

A. Fluoride of Silver.—Formed by dissolving silver-oxide or its carbonate in aqueous hydrofluoric acid, and evaporating to dryness. Hydrofluoric acid has no action on metallic silver.—Fluoride of silver is not crystalline, but fuses like horn-silver (Gay-Lussac & Thénard); on cooling, it forms a greyish black, shining, sonorous, slightly extensible mass, having a lamino-radiated fracture. (Unverdorben, *N. Tr.* 9 & 34.) When ignited for some time in the air, it becomes covered with metallic silver, and gives off hydrofluoric acid and oxygen gas; when decomposed by hydrochloric acid it yields 112·58 per cent. of chloride of silver; deliquesces in the air. (Berzelius, *Ann. Chim. Phys.* 11, 121; *Pogg.* 1, 35.)—The aqueous solution has a strongly metallic taste, blackens the skin, and is precipitated by hydrochloric acid and fixed alkalis. (Gay-Lussac & Thénard.)

By repeatedly evaporating and re-dissolving the aqueous fluoride of silver, Unverdorben obtained a substance which was no longer soluble in water, but settled down in small, soft laminæ: while moist, it exhibited a golden colour and metallic lustre; but after drying, became yellow and glistening; by pressure, it again acquired the colour and lustre of gold. Was it a basic compound?

## Silver and Nitrogen.

A. Nitrite of Silver-oxide, or Silver-nitrite.—*a. Basic?*—First obtained by Proust, who regarded it as nitrate of suboxide of silver; Hess, on the other hand, regarded it as a compound of nitric oxide with silver-oxide.—*Preparation.*—1. Aqueous silver-nitrate, boiled for several hours with finely divided silver, dissolves the metal, with evolution of nitric oxide, and forms a light yellow liquid, which, when evaporated down to a density of more than 2·4, and then kept at a low temperature for several days, solidifies suddenly on being poured into another vessel. On treating this mass with water, the salt remains undissolved in the form of a yellow powder. Cold water or alcohol likewise throws down this powder from the yellow solution. (Proust.)—2. Aqueous sulphate of silver-oxide is precipitated by nitrite of baryta (or, according to Hess, the compound of nitric oxide and baryta), and the filtrate evaporated to the crystallizing point. The baryta-salt must not be previously freed from excess of baryta by sulphuric acid, otherwise a more neutral salt will be formed, which cannot be obtained in the crystalline state. (Hess.)—3. Aqueous nitrate of silver-oxide is precipitated by nitrite of baryta. (Peligot, *Ann. Chim. Phys.* 77, 68.) Yellow powder (Proust), long, straw-yellow needles (Hess); anhydrous crystals (Peligot). Blackens on exposure to light. (Hess.) Blackens in the air, being resolved into metallic silver and nitrate. When gently heated in a glass tube, it is

resolved into metallic silver and nitrous [hyponitric?] acid. According to Peligot, it gives off nitric acid when heated, and the residue is thereby converted into nitrate of silver-oxide. When immersed in hydrochloric acid, it is superficially converted, with slight evolution of gas, into chloride of silver. Dissolves very sparingly, and only partially in water, flakes remaining behind. Easily soluble in ammonia. (Hess, *Pogg.* 12, 261.)

*b. Monobasic.*—Prepared by the process described on page 382, vol. II. White, crystalline. In contact with a chloride of an alkali-metal and water, it yields chloride of silver and an alkaline nitrite. Dissolves in 120 parts of cold water, more abundantly in hot water, and crystallizes from the hot solution on cooling. (Mitscherlich, *Lehrbuch.*) ¶ According to Fischer (*Pogg.* 74, 115), the salt thus prepared forms prisms of 59° with oblique terminal faces; it requires 300 pts. of cold water to dissolve it, but is more soluble in cold water; insoluble in alcohol. According to Persoz (*Ann. Pharm.* 65, 177), nitrate of silver-oxide may be prepared in a similar manner to the alkaline nitrites, by the action of heat on the nitrate :

$$AgO,NO^5 = AgO,NO^3 + O^2.$$

It is possible, however, to convert the whole of the nitrate into nitrite by this means; for the latter salt is only formed in presence of a nitrate, such as that of silver-oxide or potash. The best mode of obtaining it is to fuse together equal parts of nitre and silver-nitrate, dissolve the fused product in boiling water, and leave the solution to cool; the nitrite of silver-oxide is then obtained in long and very slender needles, having a wavy lustre; they are colourless while immersed in the liquid, but acquire a slight sea-green tint when taken out. They contain 69·86 per cent. of silver, a quantity nearly corresponding with the formula $AgO,NO^3$, which requires 70·13 per cent. ¶

The yellow liquid obtained by boiling finely divided silver with a solution of that metal, appears to contain a mixture of the salts *a* and *b*. According to Proust, it exhibits the following relations. When boiled down by itself, it gives off a small quantity of nitric oxide gas, then fuses, and yields a yellow sublimate. The mass treated with water when cold, yields nitrate of silver-oxide, and leaves a mixture of metallic silver and a yellow powder. The yellow solution oxidizes when exposed to the air, and deposits crystals of nitrate; the same result is produced by heating it with nitric acid, the liquid being then decolorized, and giving off nitric oxide gas. Hydrochloric acid added to the liquid, throws down white chloride of silver. Ammonia precipitates black pulverulent silver, and retains silver-oxide in solution. Potash forms a brown precipitate [of suboxide of silver] which is converted into the protoxide on exposure to the air, but, if immediately dissolved in cold dilute nitric acid, again gives a black precipitate with ammonia. Cold water added to the yellow liquid, throws down the yellow powder *a*; but on dropping the yellow liquid into boiling water, the precipitate changes colour from yellow to red, and is then converted into black metallic silver, which forms a specular deposit on the sides of the vessel. So long as the precipitate remains yellow or red, it disappears on the addition of nitric acid; but after it has become black, nitric acid no longer dissolves it. Alcohol likewise throws down the yellow powder, and the liquid filtered from it leaves, on evaporation, a residue of silver-nitrate and metallic silver. Tincture of sulphate of indigo is decolorized by the yellow liquid, with precipitation of silver.

Tincture of litmus forms with it a blue, and tincture of cochineal a violet precipitate. (Proust, *N. Gehl.* 1, 520.)

Aqueous silver-nitrite, if free from nitrate, and kept from contact of air, is not reduced by tin, nickel, bismuth, or antimony; but if nitrate is also present, reduction takes place, not only from the latter, but also from the nitrite. (Fischer, *Pogg.* 22, 496.)

B. Nitrate of Silver-oxide, or Silver-nitrate.—*Nitrate of Silver, Silver-saltpetre*, also, but improperly, called *Silver-vitriol;* after fusion, *Lunar Caustic, Lapis infernalis.*—Silver dissolves in pure dilute nitric acid, especially on the application of heat, the solution being tolerably rapid, and attended with evolution of nitrous gas. The colourless solution, when evaporated and cooled, deposits the salt in the anhydrous state.

From silver containing copper, a pure salt may be obtained by the following processes:—1. The impure silver is purified by one of the methods already described (pp. 135, 136), and the pure metal dissolved in nitric acid; or the chloride of silver, precipitated and washed, is decomposed, according to Gregory's method, by strong boiling potash-ley, and the resulting silver-oxide, after being washed, is dissolved in dilute nitric acid.—2. The impure silver is dissolved in nitric acid, the solution evaporated, and the easily crystallizing silver-nitrate is separated from the deliquescent cupric nitrate by repeated crystallization and washing with a small quantity of cold water. The water always takes up a little of the silver-salt, together with the copper-salt. If the solution contains excess of acid, the silver-nitrate separates out completely, and, according to Guibourt (*J. Chim. Méd.* 7, 536), may be washed on a funnel with strong nitric acid, in which it is almost insoluble, whereas the cupric nitrate dissolves with facility. The wash-liquid serves to dissolve a fresh quantity of silver. Another method is to evaporate the solution to dryness, taking care not to heat the residue very strongly, and then treat this residue with alcohol of 90 per cent; most of the silver-nitrate then remains undissolved, and the portion which does dissolve, separates out almost completely on cooling, while the cupric nitrate remains in the mother-liquid. (Nölle, *Ann. Pharm.* 2, 92.)—3. Part of the cupreous silver-solution is precipitated by potash, and the well-washed precipitate, consisting of hydrated cupric oxide and silver-oxide, is digested with the greater part of the solution, which, if it does not contain excess of acid, gradually deposits its cupric oxide, and dissolves out the silver-oxide from the precipitate.—4. The best method, however, is to evaporate the cupriferous silver-solution to dryness; heat the residue carefully and uniformly, in a glass, porcelain, iron, silver, or platinum dish, till it fuses, and the nitrate of cupric oxide is decomposed with intumescence; then keep the mass at the same temperature, till it fuses tranquilly, no longer exhibiting a greenish cast, and a sample of it dissolved in water, filtered, and mixed with ammoniac, no longer forms a blue solution. If the heat be too low or unequal, a portion of the cupric nitrate remains undissolved; at too high a temperature, the silver-nitrate is also decomposed and silver separated, which may be recognized by remaining behind when the cupric oxide is dissolved in sulphuric or hydrochloric acid. The mass when cold is dissolved in water, the solution filtered from the cupric oxide, and left to crystallize. (Brandenburg, *Scher. Nord. Bl.* 1, 1: *Scher. Ann.* 2, 125; Trautwein, *Repert.* 12, 153; Martius, *Repert.* 9, 319.)—If the proportion of copper is large, the residue must be merely heated

till the greater part of the cupric salt is decomposed, then dissolved in water, the filtrate evaporated to dryness, and the residue kept in a state of fusion till the remaining cupric salt is completely decomposed.

Commercial lunar caustic may be adulterated with cupric oxide, nitrate of cupric oxide, nitrate of potash, nitrate of zinc-oxide, and nitrate of lead-oxide.

Transparent and colourless crystals, belonging to the right prismatic system. *Fig.* 50: $u' : u = 129° 31'$; $p : a$ or $a' = 116° 36'$; $a' : a' = 126° 48'$; $u' : a' = 148°$. (Brooke, *Ann. Phil.* 23, 162.) Specific gravity 4·3554. (Karsten.) Fuses readily without loss of weight, and solidifies on cooling, in a white fibrous mass. Its aqueous solution does not redden litmus; it has a bitter metallic taste, and acts as an acrid poison; it destroys organic matter, and turns black when exposed to light.

| | *Crystallized.* | | Proust. | Bergman. |
|---|---|---|---|---|
| AgO | 116 | 68·23 | 69·5 | 75·19 |
| $NO^5$ | 54 | 31·77 | 30·5 | 24·81 |
| $AgO,NO^5$ | 170 | 100·00 | 100·0 | 100·00 |

108 parts of silver were found by the author to yield from 170·03 to 170·23 parts of nitrate.

Silver-nitrate does not blacken in the air, except when in contact with organic matter. At the temperature of commencing redness, it is resolved into oxygen, hyponitric acid, nitrogen, and silver. Detonates on red-hot coals. Mixed with charcoal, and struck with the hammer, it takes fire without detonation; detonates slightly with sulphur when struck with a warm hammer, and very violently with phosphorus. Decomposed by fusion with zinc, tin, cadmium, and copper; not at all, or very slowly, by the other heavy metals. (Fischer.) It is not decomposed by fusion in iron vessels, provided no water is present. (Brandenburg.) Copper reduces silver from the dry salt, even at ordinary temperatures [the air having access to it]. (Chevalier, *J. Chim. Méd.* 3, 131.) If the sublimed arsenic obtained by heating a mixture of equal parts of orpiment and iron filings be triturated with ten times its weight of silver-nitrate, a mixture is formed which takes fire immediately when shaken out upon paper. (Mauder, *Taschenb.* 1780, 36.) The crystals of the salt, if wrapped up in paper, are gradually converted, without alteration of form, into laminæ of malleable silver. (Filière, *Ann. Chim. Phys.* 42, 335.) The dry salt, triturated with excess of iodine, yields iodide of silver, free periodic acid, and nitric acid. (Preuss, *Ann. Pharm.* 29, 324.)

The salt dissolves in 1 part of cold and ½ pt. of hot water. The solution exhibits the reaction already described as belonging to silver-salts in general. Its reaction with native sulphide of antimony will be given under the head of *Silver and Antimony.* For the deoxidizing action which aqueous vapour appears to exert on silver-solutions *vid.* Pfaff (*Schw.* 36, 68; 52, 314); A. Vogel (*Gilb.* 72, 335). Alcohol, under the influence of light, very slowly reduces silver from the solution; sugar reduces it more rapidly, producing a black colour; starch, a brown; and gum a red-brown colour. (Fischer, *Kastn. Arch.* 9, 349.) For experiments on the action of various organic bodies on solution of silver-nitrate, both in the dark and under the influence of light, *vid.* Brandes & Reimann. (*N. Tr.* 12, 1, 100.) Silver-nitrate is insoluble in strong nitric acid, and is precipitated by that acid from its aqueous solution. (Schweigger-Seidel, *Schw.* 64, 127.) It forms a crystalline compound with iodide of silver. (Preuss, *Ann. Pharm.*,

29, 329.) It dissolves in 4 parts of boiling acohol. Combines with certain metallic cyanides.

*English Ink for marking on linen.* 1 pt. of lunar caustic and 1 pt. of gum-arabic dissolved in 4 parts of water, blackened with a small quantity of Indian ink. The linen to be marked is previously saturated with a solution of 1 pt. of carbonate of soda and 1 pt. of gum-arabic in 4 parts of water, and ironed smooth when dry. After marking, it is exposed to the sun for several hours, till in fact it is completely blackened. The marks may be obliterated either by repeated treatment with chlorine-water (or aqua regia) and ammonia, by which, however, the linen is injured—or better, according to Böttger, by treatment with aqueous cyanide of potassium.

C. Nitrate of Peroxide of Silver.—Peroxide of silver dissolves in nitric acid with a slight evolution of oxygen gas, and forms a brown solution, which is decolorized by deoxidizing agents, and forms permanganic acid with peroxide of manganese.

D. Compound of Silver-oxide with Ammonia.—*Argentate of Ammonia.—a. Solid.—a. Pulverulent.—Berthollet's Fulminating Silver.*—1. Silver-oxide is precipitated from a solution of the nitrate by lime-water; the adhering liquid removed by placing the precipitate on bibulous paper; and the precipitate placed in a glass vessel, and covered with very strong pure ammonia, whereupon a noise is produced like that which accompanies the slaking of lime with water. After 12 hours, the film formed upon the surface is dissolved off by fresh ammonia; the liquid decanted; and the fulminating silver collected at the bottom of the vessel, is divided into small portions, and placed upon separate pieces of bibulous paper. (Berthollet, *Crell. Ann.* 1788, 2, 390.)—2. Silver-oxide precipitated from a solution of the nitrate by a fixed alkali is cautiously boiled with a mixture of aqueous potash and ammonia. The potash withdraws any carbonic acid that may have been absorbed, and prevents the solution in excess of ammonia. (Faraday, *Quart. J. of Sc.* 4, 268; also *Ann. Chim. Phys.* 9, 107; abstr. *Pogg.* 12, 252.)—3. Recently-precipitated chloride of silver is dissolved in strong ammonia; pieces of potash-hydrate purified by alcohol (III, 13), gradually added to the solution, as long as their introduction produces effervescence; the black turbid liquid diluted with water, and thrown a filter, through which it runs colourless or yellow; and the black powder washed on the filter, and divided into small portions while still moist. (L. A. C. *J. Pharm.* 13, 615.)

Black powder, which, by slight disturbing causes, such as contact, percussion, friction, heat, or electricity, is instantly decomposed, with violent detonation, strong enough to shatter the containing vessel, the products being, apparently, metallic silver, water, and free nitrogen. In the moist state, it is much less liable to explode. The affinity of the hydrogen in the ammonia for the oxygen in the silver-oxide is much greater than that of the hydrogen for the nitrogen, or of the silver for the oxygen; slight disturbances cause the stronger affinities to get the upper hand; and then the water and nitrogen are raised by the heat developed in the formation of the water to a very high degree of elasticity. It is possible, however, that this fulminating compound may be a nitride of silver.

*β. Crystalline.* Separates from the liquid decanted off Berthollet's fulminating silver, and from every solution of silver-oxide (also of the chloride, according to Proust) in aqueous ammonia, on exposing such

solution to the air, or still more easily, on the application of heat. Black, opaque crystals, with a lustre almost metallic; they detonate with the greatest violence, on the slightest disturbance, even that which is produced by agitating the liquid in which they form. (Higgins.) The opinion of Higgins (*Minutes of a Soc. for philos. experim.* 344; also Klaproth & Wolff, *Suppl. zum chem. Wörterb.* 2, 584) regarding these crystals, appears to be correct, viz. that they are the pure fulminating silver, whereas the pulverulent substance is probably a mixture of this compound with metallic silver (and Faraday's suboxide of silver?).

*b. Liquid compound.* Regarded by Faraday as a compound of suboxide of silver with ammonia, in so far as when the oxide is dissolved in ammonia, water and nitric acid are probably formed. He did not observe any evolution of nitrogen. This compound is obtained by dissolving silver-oxide in excess of aqueous ammonia. According to Gay-Lussac, part of the oxide is always converted into fulminating silver, and remains undissolved; according to Faraday, on the contrary, the solution is perfect; according to Fischer (*Kastn. Arch.* 9, 357), the recently-precipitated oxide dissolves completely; the dried oxide only partially. The colourless solution, when exposed to the air, deposits the crystals $\beta$ (Berthollet, Higgins, Gay-Lussac), or, according to Faraday, a grey, strongly shining film of suboxide, which, when in thin layers, appears of a bright yellow colour by transmitted light, and is renewed as often as removed. If this solution be boiled for a time, it acquires a deep colour, gives off nitrogen gas, deposits fulminating silver, and becomes decolorized; on further application of heat, it blackens again, gives off nitrogen, and deposits, not fulminating silver, but the pure suboxide, which does not yield fulminating silver when treated with ammonia. The liquid argentate of ammonia, when kept for a quarter of a year in a closed vessel, deposits a thick layer of metallic silver, but no fulminating silver, and is afterwards found to contain a large quantity of oxygen gas in the compressed state. With potash, ether, and alcohol, it forms white precipitates, which soon change colour, and after drying, detonate both by heat and by friction; tincture of galls likewise precipitates argentate of ammonia abundantly. (Faraday.) From alkaline phosphates, chlorides, or chromates, the solution, if it does not contain too much ammonia, throws down all the acid, in combination with the silver-oxide. Lead and copper reduce the silver from it; tin and iron do not. (Fischer.)

E. Hyposulphite of Silver-oxide and Ammonia.—*a.* $2(NH^3,S^2O^2) + AgO,S^2O^2$?—Precipitated, on adding alcohol to the solution of chloride of silver in aqueous hyposulphite of ammonia, in the form of a white salt, which must be pressed between paper and dried in vacuo. When the remaining liquid is evaporated, an additional quantity of the salt separates out in six-sided prisms. It has a pure and very strong sweet taste, strong enough indeed to make 32,000 times its own quantity of water perceptibly sweet,—100 parts of the salt yield 40·62 parts of sulphide of silver when heated. (Herschel.) Easily soluble in water. (Herschel.)

*b.* $NH^3,S^2O^2 + AgO,S^2O^2$?—On adding to aqueous hyposulphite of ammonia a larger quantity of chloride of silver than it is capable of dissolving, a white crystalline powder is produced, which is quite insoluble in water; it must be dried in vacuo after the greater part of the water has been removed by pressure. It turns black when kept in close vessels,

and also when heated, giving off sulphurous acid and forming sulphide of silver. It dissolves in aqueous ammonia, forming an exceedingly sweet liquid, and is precipitated therefrom by acids in its original state, even when the solution is very dilute. (Herschel, *Edinb. Phil. J.* 1, 398.)

F. Sulphite of Silver-oxide and Ammonia.—Formed by dissolving silver-oxide or its sulphite in aqueous sulphite of ammonia. The solution, when exposed to sunshine, deposits a film of metallic silver, and is converted into sulphate of ammonia. (Fourcroy.)

G. Argento-hyposulphate of Ammonia. — Aqueous hyposulphate of silver-oxide supersaturated with ammonia, soon yields small crystals. (Heeren, *Pogg.* 7, 192.) The solution of hyposulphate of silver-oxide in warm ammonia yields, on cooling, small shining rhombic prisms whose four lateral edges are truncated. They turn grey when exposed to light, and when heated yield water, ammonia, sublimed sulphite of ammonia, and finally a small quantity of free sulphuric acid, and leave a residue of sulphate of silver-oxide. They dissolve in water without decomposition. (Rammelsberg, *Pogg.* 58, 298.)

| | *Crystallized.* | | | Rammelsberg. |
|---|---|---|---|---|
| $2NH^3$ | 34 | .... | 14·72 | .... 15·65 |
| AgO | 116 | .... | 50·21 | .... 49·90 |
| $S^2O^5$ | 72 | .... | 31·18 | .... |
| HO | 9 | .... | 3·89 | .... |
| $NH^3,AgO + NH^4O,S^2O^5$ | 231 | .... | 100·00 | |

H. Argento-sulphate of Ammonia.—The saturated solution of sulphate of silver-oxide in warm concentrated ammonia yields, on cooling, transparent and colourless crystals, belonging to the square prismatic system. *Fig.* 31; $p:e=127$ to 127° 13′; $q:r=135°$. The crystals are permanent in the dark, but blacken on exposure to light. They dissolve readily in water and in aqueous ammonia, and separate therefrom unaltered on cooling. From their aqueous solution, potash throws down Berthollet's fulminating silver. (C. G. & E. Mitscherlich, *Pogg.* 9, 414; 12, 140.) From the aqueous solution supersaturated with ammonia, silver is reduced by zinc, cadmium, lead, copper, antimony, and arsenic, but not by tin, bismuth, iron, or mercury. (Fischer.)

| | *Crystallized.* | | | C. G. Mitscherlich. |
|---|---|---|---|---|
| $2NH^3$ | 34 | .... | 17·90 | .... 19·40 |
| AgO | 116 | .... | 61·05 | .... 60·65 |
| $SO^3$ | 40 | .... | 21·05 | .... 21·60 |
| $NH^3,AgO + NH^3,SO^3$ | 190 | .... | 100·00 | .... 101·65 |

I. Ammonio-sulphate of Silver-oxide.—Anhydrous sulphate of silver-oxide absorbs 11·82 per cent. of ammoniacal gas, very slowly and with scarcely perceptible evolution of heat. The compound when heated, gives off ammonia, together with a small quantity of sulphite of ammonia. It dissolves completely in water. (H. Rose, *Pogg.* 20, 153.)

| | | | | H. Rose. |
|---|---|---|---|---|
| $NH^3$ | 17 | .... | 9·83 | .... 10·57 |
| AgO | 116 | .... | 67·05 | } 89·43 |
| $SO^3$ | 40 | .... | 23·12 | } |
| $NH^3 + AgO,SO^3$ | 173 | .... | 100·00 | .... 100·00 |

K. Argento-seleniate of Ammonia. — $NH^3,AgO + NH^3,SeO^3$.— Prepared like the corresponding sulphate, and isomorphous with the latter. *Fig.* 31; $p:e=127°\ 16'$. The crystals are likewise transparent and colourless, and gradually evolve ammonia when exposed to the air. They dissolve readily in water and in aqueous ammonia, and crystallize out unaltered as the ammonia evaporates; from the aqueous solution potash throws down fulminating silver. (E. Mitscherlich, *Pogg.* 12, 141.)

L. Ammonio-iodide of Silver.—Unfused iodide of silver absorbs, with evolution of heat, 3·6 per cent. of ammonia, and forms a white compound, which, on exposure to the air, gives off ammonia and turns yellow again. (Rammelsberg, *Pogg.* 48, 170.)

M. Ammonio-bromide of Silver.—Dry bromide of silver does not absorb ammoniacal gas. (Rammelsberg, *Pogg.* 55, 248.) It dissolves in strong ammonia. The solution saturated hot deposits a yellow powder on cooling. The solution becomes turbid when mixed with water, and slowly deposits white bromide of silver. Hydrosulphuric acid precipitates sulphide of silver from it. When evaporated to dryness with baryta-water, it leaves a residue from which alcohol dissolves out bromide of barium. (Berthier, *Ann. Chim. Phys.* 77, 417.) The ammoniacal solution deposits, after a while, white, shining crystals, which, when heated, are resolved into ammoniacal gas and bromide of silver. (Liebig, *Schw.* 48, 108.) The glistening laminæ which separate as the solution cools, consist of pure bromide of silver, free from ammonia. (Rammelsberg.)

N. Argento-bromate of Ammonia.—Aqueous ammonia, saturated hot with bromate of silver-oxide, yields colourless prisms on spontaneous evaporation. These crystals are decomposed in the air, even in closed vessels, becoming moist, assuming a yellowish colour, and yielding nitrogen gas, water, and bromide of silver. When heated, they are suddenly decomposed, with a hissing noise and scattering of their substance, and leave yellow bromide of silver. They are likewise decomposed by water. (Rammelsberg, *Pogg.* 52, 94.)

| | | | | | Rammelsberg. |
|---|---|---|---|---|---|
| $2NH^3$ | 34·0 | .... | 12·67 | | |
| Ag | 108·0 | .... | 40·24 | .... | 41·70 |
| O | 8·0 | .... | 2·98 | | |
| Br | 78·4 | .... | 29·21 | .... | 27·04 |
| 5O | 40·0 | .... | 14·90 | | |
| $NH^3,AgO + NH^3.BrO^5$ | 268·4 | .... | 100·00 | | |

O. Ammonio-chloride of Silver.—*a.* 100 grains of chloride of silver absorb at ordinary temperatures 130 English cubic inches of ammoniacal gas. (Faraday, *Ann. Chim. Phys.* 24, 112.)—Fused chloride of silver takes up but little ammonia; the unfused compound slowly absorbs, without evolution of heat, and with very slight increase of volume, from 17·31 to 17·91 per cent. of ammonia. (H. Rose, *Pogg.* 20, 157.) The absorbed ammonia is again given off at 37·7°. (Faraday.) When the grey compound is heated in a sealed glass tube, for the purpose of obtaining liquid ammonia, it fuses between 88° and 95°, swells up, begins to boil at 99° and gradually becomes white and anhydrous. (Niemann, *Br. Arch.* 36, 180.)

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| $3NH^3$ | 51·0 | .... | 15·1 | .... | 14·76 to 15·19 |
| 2AgCl | 286·8 | .... | 84·9 | .... | 85·24 ,, 84·81 |
| $3NH^3$,2AgCl | 337·8 | .... | 100·0 | .... | 100·00 100·00 |

*b.* When a solution of chloride of silver in strong ammonia is left to stand in an imperfectly closed vessel, ammonio-chloride of silver separates out from it in transparent and colourless rhombohedral crystals, often a quarter of inch in length. These crystals blacken when exposed to light, even while immersed in the liquid; when exposed to the air or immersed in water, they give off all their ammonia and are converted into opaque, friable chloride of silver. (Faraday.) According to Kane (*Ann. Chim. Phys.* 72, 290), white opaque, rhombic tables are produced, which immediately give off their ammonia when exposed to the air.

The solution of chloride of silver in dilute ammonia does not deposit ammonio-chloride of silver on evaporation, but pure crystallized chloride of silver. (Faraday.) The solution when heated deposits fulminating silver. (Proust.) Sulphite of ammonia boiled with it; throws down all the silver in a state of extremely minute division. (Berthier.) On passing chlorine gas through the solution, till all the ammonia is decomposed,—whereupon detonations of chloride of nitrogen are produced—the liquid yields a grey precipitate, which turns violet after the ammonia is completely decomposed, but like the white chloride of silver, contains 75 per cent. of silver, dissolves completely in ammonia, and is thrown down from it by nitric acid in the form of a white precipitate. (Cavalier, *J. Pharm.* 16, 552.) The precipitate is dark grey at first, then becomes light grey, and, after further transmission of chlorine, almost white. (Dulk, *J. pr. Chem.* 3, 237.)—Zinc and copper quickly reduce the silver from the solution in the form of a greyish black, moss-like powder; lead, slowly but completely; cadmium and antimony, slowly and incompletely; tin, iron, bismuth and mercury are without action. (Fischer.)

P. Chloride of Silver and Ammonium.—Becquerel obtained this compound by the galvanic process in octohedrons and tetrahedrons. (I. 400.) Chloride of silver dissolves in a strong solution of sal-ammoniac; so likewise does metallic silver, if the air has access to the liquid. If the air be excluded, the silver remains bright in the sal-ammoniac solution, only a trace dissolving; if the air be admitted, it turns black and dissolves, leaving only a grey dust of chloride of silver. On boiling silver in a solution of sal-ammoniac, or passing sal-ammoniac vapour over nearly red-hot silver, ammonia [and hydrogen gas?] are evolved.—A hot solution of sal-ammoniac saturated with chloride of silver yields opaque needles of that compound on cooling; a solution saturated at ordinary temperatures deposits the greater part of the silver-chloride on the addition of water. (A. Vogel, *J. pr. Chem.* 2, 197.)—Carbonate and phosphate of silver-oxide dissolve in a hot solution of sal-ammoniac. (Brett.)

Q. Argento-perchlorate of Ammonia.—The solution of silver-perchlorate in aqueous ammonia yields a crystalline compound. (Mitscherlich.)

R. Argento-nitrite of Ammonia.—The solution of silver-nitrite in warm concentrated ammonia yields this compound in large crystals on cooling. (E. Mitscherlich, *Lehrb.*)

S. Ammonio-nitrate of Silver-oxide.—Dry silver-nitrate rapidly absorbs ammoniacal gas, producing a degree of heat which causes it to fuse, and is converted, by taking up 22·55 per cent. of ammonia, into a white, coherent mass. This compound gives up its ammonia at a higher temperature. It is completely soluble in water. (H. Rose, *Pogg.* 20, 153.)

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| $3NH^3$ | 51 | .... | 23·08 | .... | 22·81 |
| $AgO,NO^5$ | 170 | .... | 76·92 | .... | 77·19 |
| $3NH^3,AgO,NO^5$ | 221 | .... | 100·00 | .... | 100·00 |

T. Argento-nitrate of Ammonia.—This compound easily separates from a solution of silver-nitrate supersaturated with ammonia. The crystals blacken when exposed to light, and are easily soluble in water. (C. G. Mitscherlich, *Pogg.* 9, 413.)—They fuse when heated, give off nitrogen gas and ammonia, and yield metallic silver, which forms a specular coating on the sides of vessel, while nitrate of ammonia remains in solution :

$$3(AgNH^2 + NH^3,HO,NO^5) = 3Ag + 2NH^3 + N + 3(NH^3,HO,NO^5).$$

(Kane, *Ann. Chim. Phys.* 72, 288.)—The first drop of ammonia added to a neutral solution of silver-nitrate, produces no precipitate, but renders the liquid strongly alkaline, without, however, imparting to it the odour of ammonia. A solution supersaturated with ammonia and evaporated to dryness, gives off nothing but the excess of ammonia, and leaves crystals of the double salt, whose solution exhibits an alkaline reaction. The same compound [probably containing free nitrate of silver-oxide?] is obtained by dissolving silver-oxide in nitrate of ammonia. (Wetzlar, *Schw.* 53, 103.)—Protosulphide of phosphorus added to the aqueous solution of this salt, throws down a blackish grey substance, chiefly consisting of sulphide of silver. (Berzelius, *Ann. Pharm.* 46, 140.)—Zinc, cadmium, tin, lead, copper, and arsenic, reduce the silver from it with the greatest rapidity, because their oxides are soluble in ammonia; mercury and antimony act less quickly; bismuth and iron not at all. (Fischer.)

| | | | | | C. G. Mitscherlich. | | Kane. |
|---|---|---|---|---|---|---|---|
| $2NH^3$ | 34 | .... | 16·67 | .... | 18·0 | | |
| $AgO$ | 116 | .... | 56·86 | .... | 55·0 | .... | 56·35 |
| $NO^5$ | 54 | .... | 26·47 | .... | 26·4 | | |
| $NH^3,AgO + NH^3,NO^5$ | 204 | .... | 100·00 | .... | 99·4 | | |

According to Kane, this compound should be regarded as $AgNH^2 + NH^3, HO, NO^5$.

Since ammonia forms soluble compounds with all silver-salts, there probably exist a greater number of double salts composed of argentate of ammonia and another ammoniacal salt; perhaps, however, the two salts often remain mixed without entering into chemical combination. According to Wetzlar, a solution of silver-oxalate in ammonia leaves silver-oxalate free from ammonia on evaporation.

## Silver and Potassium.

A. Alloy of Silver and Potassium.—Potassium acts rapidly on heated silver; water extracts potash from the compound, and leaves the

silver behind. (H. Davy.)—Serullas did not obtain any alloy of silver and potassium by igniting silver with crude tartar.

B. Argentate of Potash.—Hydrate of potash fused for 10 minutes in a silver crucible becomes yellowish, and, when dissolved in water after cooling, deposits a black mixture of silver and silver-oxide; the solution does not contain silver. (Chodnew, *J. p. Chem.* 28, 222.)

C. Carbonate of Silver-oxide and Potash.—Cold aqueous carbonate of potash dissolves a small quantity of carbonate of silver-oxide (and likewise, though still less, of chloride of silver). The solution, if heated, yields a precipitate blackened by organic matter from the filter. (Wittstein, *Repert.* 81, 145.)

D. Sulphide of Silver and Potassium.—Becquerel obtained this compound by the galvanic process (I.401, 402) in splendid prisms.

E. Hyposulphite of Silver-oxide and Potash.—When an aqueous solution of hyposulphite of soda is saturated with chloride of silver, and a strong solution of caustic potash, or of carbonate, sulphate, or nitrate of potash added to it, the double hyposulphite is precipitated in small pearly scales, which must be washed with cold water and then dried; they have a very sweet taste, fuse and turn black when heated upon charcoal before the blowpipe, and yield silver surrounded with a mass of salt; they are slightly soluble in water. (Herschel.)

F. Sulphite of Silver-oxide and Potash.—Sulphite of silver-oxide dissolves in aqueous sulphite of potash.

G. Sulphate of Silver-oxide and Potash.—Sulphate of potash fused with sulphate of silver-oxide solidifies in a crystalline mass. (H. Rose, *Pogg.* 52, 463.)

H. Iodide of Silver and Potassium.—Iodide of silver dissolves readily in cold, still more readily in hot aqueous iodide of potassium. Water and alcohol precipitate it from the solution.—*a. Bibasic.*—A concentrated solution of iodide of potassium, partially saturated while hot with iodide of silver, solidifies on cooling in a white crystalline mass, which liquefies again when heated. The crystals when pressed and dried have the composition given under *a*.

*b. Monobasic.* From a highly concentrated solution of iodide of potassium completely saturated with iodide of silver, this compound crystallizes in white needles on cooling. The analysis of these needles is given under *b*, *a*. Their solution in hot alcohol yields, on cooling, white needles, which turn yellow on drying, and blue when exposed to light. Their analysis is given under *b*, *β*. (Boullay, *Ann. Chim. Phys.* 34, 377.)—On saturating potash-ley with iodine, then evaporating, and fusing in a silver crucible, a large quantity of silver is dissolved; the solution of the mass in a small quantity of water deposits iodide of silver on the addition of a larger quantity. (Anthon, *Repert.* 43, 174.)

| | | | | Boullay. *a.* |
|---|---|---|---|---|
| 2KI | 330·4 | 58·54 | | 61·17 |
| AgI | 234·0 | 41·46 | | 38·83 |
| 2KI,AgI | 564·4 | 100·00 | | 100·00 |

| | | | | Boullay. | | | |
|---|---|---|---|---|---|---|---|
| | | | | *b*,*a*. | | *b*,*β*. | |
| KI..... | 165·2 | .... | 41·38 | .... | 41·74 | .... | 40·8 |
| AgI ..... | 234·0 | .... | 58·62 | .... | 58·26 | .... | 59·2 |
| KI,AgI..... | 399·2 | .... | 100·00 | .... | 100·00 | .... | 100·0 |

I. Chloride of Silver and Potassium.—Becquerel obtained this compound by the galvanic method (I. 401) in tetrahedrons and octohedrons. Chloride of silver behaves with chloride of potassium in the same manner as with chloride of sodium. (Wetzlar.)

¶ K. Nitrite of Silver-oxide and Potash.—Obtained by adding nitrite of potash in excess to a solution of silver-nitrate, and evaporating over sulphuric acid.—Crystallizes in rhombic prisms of about 50°, with several modifications. Yellowish, permanent in the air; resolved at a gentle heat into the silver and potash salts; if more strongly heated, and then digested in water, it yields metallic silver. The former decomposition is likewise produced by water. (Fischer, *Pogg.* 74, 115.) ¶

## Silver and Sodium.

A. Borax dissolves silver-oxide and likewise metallic silver in the outer blowpipe flame, and, on cooling, becomes opalescent or milk-white, according to the quantity; in the inner flame, it turns grey from reduction of silver. (Berzelius.)

B. With microcosmic salt, both silver-oxide and the metal form in the outer flame, a yellowish, or if the quantity of silver be considerable, an opalescent glass, which appears yellowish by transmitted day-light, and reddish by transmitted candle-light. In the inner flame it turns grey by reduction. (Berzelius.)

¶ C. Metaphosphate of Silver-oxide and Soda.—Formed by mixing a solution of silver-nitrate with excess of metaphosphate of soda, and leaving the solution to crystallize for 2 or 3 days. Beautiful transparent crystals are then formed, belonging to the oblique prismatic system. They contain 99·05 per cent. of metaphosphate of silver-oxide and 0·86 of metaphosphate of soda, corresponding to the formula $AgO,PO^5 + NaO,PO^5$.—When, on the contrary, metaphosphate of soda is mixed with a large excess of silver-nitrate, smaller crystals are formed, consisting merely of metaphosphate of silver-oxide, $3(AgO,\alpha PO^5) + 2Aq$. (See p. 150). (Fleitmann & Henneberg, *Ann. Pharm.* 65, 310 ) ¶

D. Hyposulphite of Silver-oxide and Soda.—*a*. $2(NaO,S^2O^2) + AgO,S^2O^2$.—1. Formed by evaporating a solution of silver-chloride in aqueous hyposulphite of soda at a gentle heat, till it crystallizes. The crystals are contaminated with a considerable quantity of sulphide of silver. (Herschel, *Edinb. Phil. J.* 1, 398.)—2. By saturating a concentrated solution of hyposulphite of soda with chloride of silver, which may have free acid adhering to it, till the liquid becomes turbid by deposition of a white powder, then filtering, precipitating by alcohol, washing the laminar precipitate with alcohol till the liquid which runs off contains no more chlorine, and drying it as quickly as possible in vacuo without application of heat. (Lenz.)—3. By adding a neutral

solution of silver-nitrate, drop by drop, to aqueous hyposulphite of soda till a permanent precipitate of salt *b* begins to appear, then filtering, precipitating by alcohol, and proceeding as in 2. (Lenz, *Ann. Pharm.* 40, 94.)

Silky laminæ united in tufts, and having a very sweet taste. (Herschel.) On evaporating the aqueous solution in vacuo, large laminæ are obtained; but, if the salt be precipitated from its aqueous solution by alcohol, then heated till it re-dissolves, and left to cool, fibrous needles are formed having the same composition.

The salt is not altered by air or light. At 100° it gradually becomes darker, from formation of sulphide of silver. The aqueous solution, when boiled for a long time, likewise deposits sulphide of silver and turns sour. Hydrochloric acid acts slowly on the aqueous solution at ordinary temperatures, forming a black precipitate from which ammonia extracts chloride of silver. (Lenz.)—The salt dissolves readily in water (Herschel); it is easily soluble in ammonia, and likewise, to a certain extent, in alcohol, especially if the alcohol be warm or diluted with water. (Lenz.)

| | *Crystallized.* | | | | Lenz. |
|---|---|---|---|---|---|
| $2NaO$ ..... | 62·4 | .... | 18·33 | .... | 18·44 |
| $AgO$ ..... | 116·0 | .... | 34·08 | .... | 33·50 |
| $3S^2O^2$ ..... | 144·0 | .... | 42·30 | .... | 43·01 |
| $2HO$ ..... | 18·0 | .... | 5·29 | .... | 5·05 |
| | 340·4 | .... | 100·00 | .... | 100·00 |

*b.* $NaO,S^2O^2 + AgO,S^2O^2$.—1. The above solution of chloride of silver in hyposulphite of soda, when cooled after the salt *a* has separated from it, yields small, hard, strongly shining, flat, six-sided prisms, bevelled with two faces. They have a sweet taste, fuse when heated, turning black and yielding sulphide of silver, and are slightly soluble in water. (Herschel.)—2. The same compound is obtained by adding a neutral solution of silver-nitrate to aqueous hyposulphite of soda, as long as a precipitate forms. The precipitate, which is flocculent at first, soon becomes crystalline, turns somewhat brown in washing, and after drying, assumes the appearance of a dingy white crystalline powder. It turns black when boiled with water, or on exposure to the air, and is then no longer soluble in hyposulphite of soda, although in the undecomposed state it dissolves completely in that salt, forming a solution which contains the salt *a*; in its original state, it is likewise easily soluble in ammonia, but sparingly in water. (Lenz.)

| | *Crystallized.* | | | | Lenz. |
|---|---|---|---|---|---|
| $NaO$..... | 31·2 | .... | 12·37 | .... | 12·29 |
| $AgO$..... | 116·0 | .... | 46·00 | .... | 45·68 |
| $2S^2O^2$ ..... | 96·0 | .... | 38.06 | .... | 38·20 |
| $HO$ ..... | 9·0 | .... | 3·57 | .... | 3·83 |
| | 252·2 | .... | 100·00 | .... | 100·00 |

E. Sulphite of Silver-oxide and Soda.—Analogous to the potash-compound.

F. Chloride of Silver and Sodium.—1. Fused chloride of sodium dissolves chloride of silver; and the mixture solidifies at a dull red heat, forming a transparent, slightly coloured glass, which has a saline, non-metallic taste, turns violet on exposure to light, and is decomposed by water. (Boussingault, *Ann. Chim. Phys.* 54, 261.)—2. By saturating a

strong boiling solution of chloride of sodium with precipitated chloride of silver, a solution of chloride of silver and sodium in aqueous chloride of sodium is obtained, from which the double chloride crystallizes on cooling, mixed, however, with a small quantity of free chloride of sodium.—A more dilute solution of common salt likewise takes up chloride of silver on boiling, but deposits it again unchanged on cooling, inasmuch as the excess of water exerts a decomposing action on the double chloride.—Cubes, which are undistinguishable from those of common salt, and do not blacken when exposed to light. When immersed in water, they are resolved into chloride of silver and a dilute solution of common salt. With an almost saturated solution of common salt, the double chloride forms a solution, from which water throws down chloride of silver, but which is not precipitated either by green vitriol or by potash. (Wetzlar, *Schw.* 51, 371; 53, 97.)—3. Becquerel obtained this compound by the galvanic process in tetrahedrons and octohedrons. (I. 401.)

¶ G. Nitrite of Silver-oxide and Soda.—Analogous to the nitrite of silver-oxide and potash. (Fischer.) ¶

## Silver and Barium.

A. Alloy of Silver and Barium.—*a.* Clarke (*Gilb.* 62, 373), by heating silver and baryta together before the oxy-hydrogen blowpipe, obtained a greyish-white, strongly shining, hard, and very malleable alloy, which fell to powder when exposed for a while to the air.—*b.* Lampadius (*Schw.* 15, 146), by exposing a mixture of 4 pts. silver, 4 baryta, and 1 charcoal-powder, to a white heat, obtained an alloy which, on exposure to the air, was reduced to a powder consisting of baryta and silver-oxide [?].

B. Chloride of Silver and Barium.—Obtained by the galvanic process in octohedrons and tetrahedrons. (Becquerel.)

¶ C. Nitrite of Silver-oxide and Baryta.—Analogous to the potash-salt. (Fischer.) ¶

## Silver and Strontium.

Hyposulphite of Silver-oxide and Strontia.—Chloride of silver immersed in an aqueous solution of hyposulphite of strontia, is converted into a white powder, very slightly soluble in excess of hyposulphite of strontia, but easily in ammonia, with which it forms an intensely sweet liquid. (Herschel.)

## Silver and Calcium.

A. Hyposulphite of Silver-oxide and Lime.—*a.* Aqueous hyposulphite of lime, saturated with chloride of silver, forms, on agitation with a large quantity of alcohol, a white precipitate, which must be washed with alcohol till all the chloride of calcium is removed, then pressed, and dried in vacuo.—White, very sweet, easily soluble in water,

with the exception of a residue arising from decomposition during drying. (Herschel.)

*b.* When to a solution of hyposulphite of lime already saturated with chloride of silver, a further quantity of that compound is added, the latter is immediately converted into a bulky, white, crystalline powder. The wash-water, evaporated at a gentle heat, yields very oblique prisms of the double salt. This compound decomposes slightly when kept. It dissolves very sparingly in water, but abundantly in ammonia, with which it forms a very sweet liquid. (Herschel.)

B. Chloride of Silver and Calcium.—Chloride of silver dissolves in a strong solution of chloride of calcium. (Wetzlar.)

## Silver and Silicium.

A. Alloy of Silicium and Silver.—Silver heated with silicium before the blowpipe, forms a malleable alloy, which dissolves in acids, leaving a small residue of silica. (Berzelius, *Pogg.* 1, 220.)

B. Carbide of Silicium and Silver.—Silver, mixed with silica and lamp-black, and exposed to the heat of a forge, takes up a certain quantity of silicium and carbon. (Stromeyer.)

C. Fluoride of Silicum and Silver.—$AgF,SiF^2$.—A solution of silver-oxide in hydrofluosilic acid, yields granular crystals, which deliquesce in the air. Ammonia added to the solution throws down a light yellow *basic salt*, which, when treated with excess of ammonia, is converted into *Silicate of Silver-oxide.*

D. Silver-oxide imparts a yellow colour to glass fluxes.

## Silver and Tantalum.

Tantalate of Silver-oxide.—White, insoluble precipitate.

## Silver and Tungsten.

A. Alloy of Silver and Tungsten.—Pale brown alloy, somewhat spongy and malleable. (De Luyart.)

B. Tungstate of Silver-oxide, or Silver-tungstate.—*Bi-acid.*—Alkaline bitungstates added to solution of silver-nitrate, throw down an anhydrous white powder. This powder turns brown when gently heated, greenish-brown at a stronger heat, and at a bright red heat is converted into a coherent mass having the metallic lustre. In the unignited state, it does not dissolve in water, scarcely at all in phosphoric or acetic acid, more readily in ammonia and in potash, and with a brownish colour in oxalic acid. (Anthon, *J. pr. Chem.* 9, 347.)

| | | | | | Anthon. |
|---|---|---|---|---|---|
| $AgO$ | 116 | .... | 32·58 | .... | 31 |
| $2WO^3$ | 240 | .... | 67·42 | .... | 69 |
| $AgO,2WO^3$ | 356 | .... | 100·00 | .... | 100 |

C. Sulphotungstate of Silver.—$AgS,WS^3$.—Dark brown precipitate which soon turns black, gives off sulphur when distilled, and leaves a lead-grey residue. (Berzelius.)

## Silver and Molybdenum.

A. Alloy of Silver and Molybdenum.—1 pt. of silver forms 2 parts of molybdenum, a grey, granular, brittle alloy.

B. Molybdate of Silver-oxide, or Silver-molybdate.—Molybdate of potash forms with nitrate of silver-oxide, a greenish-white precipitate, slightly soluble in water. (Richter.)—Molybdic acid forms with nitrate of silver-oxide, a white, flaky precipitate. (Scheele.) This precipitate is slightly soluble in nitric acid. (H. Rose, *Pogg.* 40, 400.)

¶ *Monomolybdate.*—Neutral molybdate of potash forms with nitrate of silver-oxide, a yellowish-white, flocculent precipitate, which darkens when exposed to light. It is sparingly soluble in pure water, but dissolves readily in water containing nitric acid. (Svanberg & Struve, *Ann. Pharm.* 68, 299.)

| | *Dried at* 100°. | | | Svanberg & Struve. |
|---|---|---|---|---|
| AgO | 116 | .... | 62·34 | .... 61·33 |
| $MoO^3$ | 72 | .... | 37·66 | .... 38·67 |
| $AgO,MoO^3$ | 188 | .... | 100·00 | .... 100·00 |

*b. Acid Molybdate.*—Termolybdate of potash forms with nitrate of silver-oxide, a flocculent, yellowish-white precipitate of somewhat variable composition, but agreeing best with the formula, $AgO,3MoO^3 + AgO,2MoO^3$.

| | | | | Svanberg & Struve. |
|---|---|---|---|---|
| 2AgO | 232 | .... | 39·19 | .... 39·75 to 41·14 |
| $5MoO^3$ | 360 | .... | 60·81 | |
| $AgO,3MoO^3 + AgO,2MoO^3$ | 592 | .... | 100·00 | |

(Svanberg & Struve, *Ann, Pharm.* 68, 299.) ¶

C. Sulphomolybdate of Silver.—$AgS,MoS^3$.—Black precipitate, which, after drying, is rendered lead-grey and shining by pressure. (Berzelius, *Pogg.* 7, 277.)

D. Persulphomoybdate of Silver.—$AgS,MoS^4$.—Very dark brown precipitate, which turns black when collected. (Berzelius, *Pogg.* 7, 288.)

## Silver and Vanadium.

Vanadiate of Silver-oxide, or Silver-vanadiate.—*a. Monobasic.*—Neutral nitrate of silver-oxide, decomposed by monovanadiate of ammonia, yields a white or pale yellow precipitate. When the silver-solution is mixed with powdered vanadiate of ammonia, the precipitate formed is yellow at first, but turns white after being stirred for some time; and if the mixture be warmed or left to stand for 24 hours, becomes yellow again, though paler than at first. If the silver-solution be pre-

cipitated by the dissolved ammonia-salt, the precipitate obtained is yellow and very gelatinous. (Berzelius.)

*b. Bivanadiate.*—Aurora-red; fuses below a red heat and crystallizes on cooling. Slightly soluble in water, easily in nitric acid and in very dilute ammonia. The latter solution is pale yellow, and when left to spontaneous evaporation, yields crystals of an ammoniacal double salt. (Berzelius.)

## Silver and Chromium.

Chromate of Silver-oxide, or Silver-chromate.—*a. Monochromate.*—Silver-oxide abstracts chromic acid from aqueous monochromate of potash, leaving the liquid alkaline; even a large excess of the oxide does not remove the whole of the acid, unless it is added in the state of ammoniacal solution. (Fischer, *Kastn. Arch.* 9, 351.)—1. This compound remains, on boiling the bichromate of silver-oxide with water, in the form of a dark green, crystalline mass, which appears green by transmitted light, but yields a red powder. (Warington.)—2. The solution of the bi-acid salt in aqueous ammonia, becomes covered, if left to spontaneous evaporation, with a dark-green, metallic-looking crust of the monochromate, which appears red by transmitted light, and yields a red powder. (Warington, *Phil. Mag. J.* 11, 489; also *Ann. Pharm.* 27, 12; also *J. pr. Chem.* 12, 338.) The product thus obtained consists of scales, laminæ, or fine needles (Hayes likewise obtained needles), of a brown, yellowish-brown, or greenish-brown colour, dark red by transmitted light, immediately converted into chloride of silver by hydrochloric acid, common salt, or sal-ammoniac, insoluble in water, but soluble in acids, ammonia, and chromate of potash. (Fisher, *Kastn. Arch.* 9, 355.)

| | | | | Warington (1). |
|---|---|---|---|---|
| $AgO$ | 116 | 69·05 | | 68·57 |
| $CrO^3$ | 52 | 30·95 | | 30·76 |
| $AgO,CrO^3$ | 168 | 100·00 | | 100·00 |

The precipitate obtained by adding monochromate of potash to a neutral solution of silver-nitrate probably also belongs to this head, although it exhibits no green colouring.—This precipitate is of a deep purple-red colour, finely crystalline, and darkens when exposed to light. In the outer blowpipe flame, it fuses to a bead which exhibits the metallic lustre, but still yields a purple powder; in the inner flame it is reduced to chromic oxide and metallic silver. (Vauquelin.) Several metals, when immersed for some time in water in contact with silver-chromate, exert a reducing action upon it. (Vauquelin.) Cadmium separates pure silver; zinc separates black-brown, arborescent silver mixed with chromium [?]; tin, lead, and iron, a brown spongy powder, probably containing chromate of silver-oxide as well as metallic silver; and arsenic, a powder having more of a green tinge, arising from the presence of chromic oxide; copper and mercury act very feebly upon it; tin and antimony not at all. When decomposition takes place, the water acquires a yellow tinge, from the presence of chromic acid. (Fischer, *Pogg.* 8, 488.)—Monochromate of silver-oxide is decomposed by hydrochloric acid, hydrochlorates, and sulphates. (Hayes.) It is insoluble in water, but dissolves in acids, alkalis, and alkaline chromates. (Fischer, *Kastn. Arch.* 9, 355.)

*b. Bichromate.*—1. A plate of silver immersed in an aqueous solution

of 3 pts. bichromate (or monochromate) of potash, and from 3 to 4 pts. of oil of vitriol, becomes covered with scarlet crystals. The crystalline film must be frequently removed, otherwise it will interfere with the action. The silver is oxidized at the expense of part of the chromic acid, which, being reduced to chromic oxide (part of which forms chrome-alum), colours the liquid first brown and then green. (Warington.) The formation of the crystals is remarkably accelerated by the heat of the summer sun. (Zeller, *Repert.* 71, 250.) Helmsauer (*Repert.* 38, 105), had previously obtained crystals in this manner, from an aqueous mixture of sulphuric and chromic acids with silver; but he regarded them as composed of sulphate and chromate of silver-oxide.—2. The same compound is obtained on mixing a solution of silver-nitrate with bichromate of potash. Warington uses an acid solution of silver-nitrate, and obtains a purple-red crystalline precipitate. Zeller boils the mixture for a while, filters, and in that way obtains crystals. It had been previously observed by Vauquelin, that the precipitate formed by monochromate of potash in an acid solution of silver-nitrate, has a particularly fine red colour; and the same was observed by Moser in the precipitate obtained with the silver solution and bichromate of potash. From a mixture of [acid?] solution of silver-nitrate and chromate of potash, filtered from the precipitated silver-chromate, Teschemacher obtained, after leaving the liquid to stand for a long time, distinct crystals, which will be presently described.—3. A mixture of silver-nitrate and chromic acid yields ruby-red crystals. (Moser.)—4. The solution of the monobasic salt in nitric acid yields red crystals on evaporation. (Vauquelin.)—5. Rhombic tables are likewise obtained by evaporating the solution of the salt in warm water; they are dark brown by reflected, and carmine-coloured by transmitted light (Warington); steel-grey by reflected, ruby-red by transmitted light. (Moser.)—6. The filtrate obtained by boiling the salt with water, deposits the salt in red micaceous laminæ on cooling. (Warington.)

The salt crystallizes in laminæ and prisms belonging to the doubly oblique prismatic system. *Fig.* 121: $y : u = 69° 55'$; $y : v = 123°$; $u : v = 101° 5'$. They have a strong metallic lustre, and appear dark red by transmitted light, like Red Silver-ore. (Teschemacher, *Phil. Mag. Ann.* 1, 345; also *Schw.* 50, 254.) The salt prepared by (1) forms scarlet rhombic laminæ, often with two truncated summits (Warington); ruby-red transparent prisms (Helmsauer); by (2), on mixing the solutions hot, and leaving the filtrate to cool: shining, carmine-coloured, micaceous laminæ (Zeller); by (2), the liquids being mixed cold; carmine-coloured crystalline powder (Vauquelin), which, when examined by the microscope, is found to consist of rhombic laminæ (Moser):

| | *Crystallized* (1.) | | Warington. |
|---|---|---|---|
| AgO..... | 116 .... | 52·73 .... | 52·95 |
| $2CrO^3$ ..... | 104 .... | 47·27 .... | 46·80 |
| $AgO,2CrO^3$ ..... | 220 .... | 100·00 .... | 99·75 |

The salt heated before the blowpipe yields an emerald-green bead (Teschemacher); when strongly ignited, it yields chromic oxide and metallic silver. (Helmsauer.) It dissolves sparingly in water, forming a bright yellow solution, which reddens litmus, and yields crystals on evaporation. When boiled with water, it is resolved into dark green monochromate of silver-oxide and an acid solution, which, on cooling, again yields crystals of bichromate of silver-oxide. It is easily soluble in nitric acid and ammonia. (Warington.)

B. Argento-chromate of Ammonia.—$NH^3,AgO+NH^3,CrO^3$.—Formed by dissolving chromate of silver-oxide in warm concentrated ammonia, and leaving the solution to crystallize by cooling. Yellow, transparent crystals, isomorphous with those of the argento-sulphate and argento-seleniate. *Fig.* 31: $p : e = 127° 47'$.—When exposed to the air it gives off ammonia much more quickly than the argento-seleniate, and gradually acquires a red colour. Potash added to its aqueous solution, throws down fulminating silver. (E. Mitscherlich, *Pogg.* 12, 141.) From a solution of silver-chromate in ammonia, zinc throws down metallic silver and chromium; cadmium precipitates nothing but silver; copper quickly precipitates a grey powder, probably a mixture of silver and chromic oxide; lead throws down pure silver at first, but afterwards a black dendritic powder. In this reaction, the ammonia, if not in excess, does not dissolve a trace of the precipitating metal. Tin, iron, and mercury, have no action on the salt. (Fischer, *Kastn. Arch.* 8, 488.)

## Silver and Uranium.

Uranate of Silver-oxide.—1. Ammonia added, not in excess, to an aqueous mixture of uranic nitrate and excess of silver-nitrate, throws down a yellowish red compound, which, after drying in vacuo, may be heated without undergoing any change beyond the loss of a trace of water, and contains a quantity of silver-oxide, varying from 24·65 to 27·89 per cent. (Rammelsberg, *Pogg.* 59, 10.)—2. Acetate of uranic oxide and silver-oxide yields uranate of silver-oxide when boiled with water. The latter becomes light brown on ignition, and is decomposed by hydrochloric acid, yielding chloride of silver and hydrochlorate of uranic oxide. (Wertheim, *J. pr. Chem.* 29, 221.)

## Silver and Manganese.

Permanganate of Silver-oxide.—A warm solution of permanganate of potash, mixed with solution of silver-nitrate, yields, on cooling, large, anhydrous crystals, belonging to the oblique prismatic system. *Fig.* 88: $u' : u = 112° 7'$; $i : u = 92° 12'$. They dissolve in 109 pts. of cold water, in a much smaller quantity of hot water, and may be recovered by gentle evaporation, though decomposition takes place on boiling. (Mitscherlich, *Pogg.* 25, 301.)

## Silver and Arsenic.

A. Arsenide of Silver.—According to Gehlen, 100 parts of pulverulent silver, heated with an equal quantity of arsenic, take up, without visible combustion, about 16 parts of the latter, and form a compact, steel-grey, brittle, fine-grained mass. According to Bergman, silver in the fused state takes up $\frac{1}{14}$th of its weight of arsenic, becoming yellow and brittle. Silver and chloride of silver do not act upon arsenious acid at high temperatures. (Gehlen.)

B. Arsenite of Silver-oxide, or Silver-arsenite.—Arsenite of potash or ammonia throws down a yellow powder from solution of silver-nitrate. Free arsenious acid produces only a white turbidity, the yellow

precipitate appearing only on the cautious addition of the alkali. The yellow powder turns brown on exposure to light. When dried at a gentle heat, it still remains yellow; if it be then more strongly heated, it turns black, still giving off a small quantity of water and arsenious acid (according to Marcet, a dark brown basic salt is produced). On igniting it in a glass-tube till the glass softens, a larger quantity of arsenious acid sublimes, and the residue is a mixture of silver free from arsenic, and arseniate of silver-oxide. (Simon, *Pogg.* 40, 419.) The salt heated on charcoal before the blowpipe, yields a globule of silver. It is insoluble in water, but dissolves in acids, in nitric acid, for instance, and when recently precipitated, also in ammonia. (Marcet, *Ann. Phil.* 3, 236; also *Schw.* 13, 110.) It dissolves in acetic acid more readily than the phosphate of silver-oxide. (H. Rose.) It dissolves imperfectly, leaving a dingy yellow residue, in carbonate, sulphate, and nitrate of ammonia; by immersion in a solution of sal-ammoniac, it is converted into chloride of silver. (Wittstein, *Repert.* 51, 41.) Arsenite of silver-oxide is not converted into arseniate, even by repeated boiling with nitric acid. (Laugier & Pelletier, *J. Pharm.* 11, 387.)

¶ By pouring a solution of arsenious acid into an ammoniacal solution of silver-nitrate, Filhol obtained a salt, having the composition, $3AgO, AsO^3$. This salt is of a siskin-yellow colour, soon turning green on exposure to light. It is difficult to deprive it of the whole of its water; at 140°—150°, it suddenly assumes a fine black tint, and loses only 0·2 per cent. in weight; at a stronger heat it fuses, and gives off arsenious acid. (Filhol, *Ann. Pharm.* 68, 311.) ¶

C. Arseniate of Silver-oxide, or Silver-arseniate.—*a. Terbasic.*—Formed by precipitating a solution of silver-nitrate with arsenic acid, or with monobasic, bibasic, or terbasic arseniate of ammonia, potash, or soda.—Arsenic acid and mono-arseniate of potash precipitate silver-oxide imperfectly, because the acid which is set free retains part of the salt in solution. (Scheele.) When a bibasic alkaline arseniate is used, the supernatant liquid becomes acid (Mitscherlich); with a terbasic salt it remains neutral. (Graham.)—The precipitate carries down with it a small quantity of silver-nitrate, which cannot be completely removed by washing; but if the liquid contains nitrate of ammonia, no nitrate of silver-oxide mixes with the precipitate; moreover, the latter, when brought in contact with a pure solution of silver-nitrate, does not take up any of it; hence it would appear, that arseniate of silver-oxide can only take up the nitrate at the very instant of precipitation. (Graham.)—Dark brown-red precipitate.—When heated in a retort till the glass softens, it fuses without decomposition, and forms a brown mass, translucent at the edges; by still stronger ignition in a covered crucible, it yields metallic silver. (Scheele.) On charcoal before the blowpipe, it yields arsenical silver. (Simon.)—Hydrochloric acid converts it into chloride of silver. It is insoluble in water, but dissolves in aqueous ammonia. (Scheele, *Opusc.* 2, 52.)—Dissolves readily in carbonate of ammonia, but not in sulphate, nitrate, or succinate of ammonia, even on the application of heat. (Wittstein.) Dissolves very sparingly in nitrate of ammonia, more freely in acetic acid. (Graham.)

| | | | Smithson. |
|---|---|---|---|
| $3AgO$ | 348 | 75·16 | 76·69 |
| $AsO^5$ | 115 | 24·84 | 23·31 |
| $3AgO,AsO^5$ | 463 | 100·00 | 100·00 |

*b. Acid Arseniate.*—Aqueous arsenic acid has no action on silver; but when the acid is fused with silver, arsenious acid sublimes, and there is formed a nearly transparent, colourless glass, from which water extracts arsenic acid, together with a small quantity of silver-oxide, leaving behind the brown-red salt *a.* (Scheele.)

D. Sulpharsenite of Silver.—*a. Twelve-basic.*—12 AgS, $AsS^3$.—The yellow precipitate formed on mixing an ammoniacal solution of chloride of silver with excess of solution of orpiment in aqueous potash. If the chloride of silver solution is in excess, nothing but sulphide of silver separates out. (Berzelius.)

*b. Terbasic.*—3 AgS, $AsS^3$.—Found native in the form of *Light Red Silver.*—3 At. sulphide of silver unite by fusion with 1 At. of tersulphide of arsenic, the action being attended with evolution of light and heat; and form a translucent, cochineal-coloured mass. This mass, when fused in an atmosphere of hydrogen, gives off first sulphide of arsenic, and then pure arsenic; it then solidifies, and does not readily part with the last portions of arsenic. (Wöhler, *Ann. Pharm.* 27, 159.)

*Light Red Silver, Arsenical Silver-blende.*—Crystalline system, the rhombohedral. Primary form, an obtuse rhombohedron, *Fig.* 141; $r^3 : r^5 = 107° 36'$; *Fig.* 135, 145, 148, 158, and other forms. A little harder than rock-salt. Sp. gr. from 5·53 to 5·59. Semi-transparent, with an adamantine lustre; cochineal or carmine-coloured; streak aurora-red. Fuses on charcoal before the blowpipe, diffusing an odour of arsenic and sulphurous acid, and forming a black, brittle, metallic bead, which yields a button of pure silver, with difficulty when fused alone, but easily when treated with carbonate of soda. Potash-ley blackens the powder by dissolving out the sulphide of arsenic. Hot nitric acid also blackens the powder, and dissolves it partially, leaving a residue of sulphur and arsenious acid.

| | *Light Red Silver.* | | | H. Rose. From Joachimsthal. |
|---|---|---|---|---|
| 3Ag | 324 | .... | 65·45 | .... 64·67 |
| Sb | | .... | | .... 0·69 |
| As | 75 | .... | 15·15 | .... 15·09 |
| 6S | 96 | .... | 19·40 | .... 19·51 |
| $3AgS,AS^3$ | 495 | .... | 100·00 | .... 99·96 |

On the *Xanthotone* associated with light red silver, *vid.* Breithaupt & Plattner. (*J. pr. Chem.* 20, 7.)

*c. Bibasic.*—2 AgS, $AsS^3$.—Formed by heating *d.*—Black metallic mass, yielding a light brown powder, which is not altered by heating out of contact of air.

*d. Monobasic.*—AgS, $AsS^3$.—A saturated solution of orpiment in hydrosulphate of soda forms with nitrate of silver-oxide a light brown precipitate, which soon turns black, and, when heated in close vessels, gives off orpiment, then fuses, afterwards gives off more orpiment, and is converted into *c.* (Berzelius, *Pogg.* 7, 150.)

E. Sulpharseniate of Silver.—3AgS, $AsS^5$ and 2AgS, $AsS^5$.—Both the terbasic and the bibasic sulpharseniate of sodium, when added to a silver-solution, first colour it dark brown, and then throw down a black mass which yields a brown powder. This substance, when heated in the air, is converted into sulphide of silver by the combustion of the sulphide of arsenic, but, if heated to redness in a close vessel, fuses, without

evolving sulphur or sulphide of arsenic, and, on cooling, solidifies in the form of a grey, somewhat ductile cake, exhibiting the metallic lustre. (Berzelius, *Pogg.* 7. 29.)

## Silver and Antimony.

A. Antimonide of Silver.—Found native.—1. By fusing the two metals together, a silver-white, brittle alloy is obtained, whose specific gravity is less than the mean of the constituent metals. When heated in the air it gives off antimony, which oxidizes and volatilizes. Nevertheless, according to Bonsdorff, 0·1 per cent. of antimony remains obstinately combined with the silver, and gives it a dull, greyish look; it may, however, be removed by cupellation with lead.—2. When a solution of silver-nitrate is precipitated by antimony, broad, brittle, shining laminæ of antimonide of silver are formed towards the end of the action; the alloy thus obtained does not fuse at a strong red heat, because the antimonious acid which forms disposes itself between the particles of the silver, and prevents their union, till it is volatilized by continued blowing. (Fischer, *Pogg.* 10, 606; *Kastn. Arch.* 13, 224.)

*Native Antimonide of Silver.*—Crystalline system the rhombohedral. Six-sided prisms with truncated lateral edges. Scalenohedrons (*Fig.* 147). similar to those of calcspar. (Breithaupt, *Pogg.* 7, 527; *Schw.* 52, 169.) Specific gravity from 9·4 to 9·8. Harder than calcspar. Silver-white. Fuses readily on charcoal before the blowpipe, giving off an antimonial fume, which stains the charcoal, and is reduced to a grey, brittle, metallic globule, which becomes white after longer blowing, and solidifies, with incandescence, to a crystalline globule on cooling; by still longer blowing, it is converted into pure metallic silver. Heated in a tube, it yields a sublimate of antimonic oxide, and becomes covered with yellow, vitrified antimonic oxide. (Berzelius.)—In contact with nitric acid, it is resolved into a solution of silver-nitrate, and undissolved antimonic nitrate.

| | *Antimonide of Silver.* | | | Klaproth. | | | | | Klaproth. |
|---|---|---|---|---|---|---|---|---|---|
| | At. | | | *a.* | *b.* | At. | | | *c.* |
| Ag..... | 4 | 432 | 77·01 | 76 | 77 | 6 | 648 | 83·4 | 84 |
| Sb..... | 1 | 129 | 22·99 | 24 | 23 | 1 | 129 | 16·6 | 16 |
| $Ag^4Sb$.. | | 561 | 100·00 | 100 | 100 | $Ag^6Sb$ | 777 | 100·0 | 100 |

*a.* is coarse-grained antimonide of silver from Wolfach; *b*, a lamino-granular variety from Andreasberg; *c*, fine-grained from Wolfach.

B. Antimoniate of Silver-oxide.—White precipitate, insoluble in water. (Berzelius.)

C. Sulphantimonite of Silver.—*a. Polybasite.*—$2\,AgS, SbS^3$.—Part of the silver is replaced by copper, and part of the antimony by arsenic.—Regular, six-sided prisms, perpendicularly truncated. Specific gravity of the ore from Durango = 6·214. Fracture uneven, without cleavage-planes. Harder than rock-salt. Has a strong lustre and iron-black colour, and yields a powder of the same tint. (H. Rose, *Pogg.* 15, 573; 28, 156.) Decrepitates slightly before the blowpipe; fuses very easily, yielding sulphurous acid and a film of antimony, sometimes also an arsenical fume, especially when fused with carbonate of soda; colours glass-fluxes in the same manner as copper.

| | At. | | | H. Rose. *a.* |
|---|---|---|---|---|
| Zn | | | | |
| Fe | | | | 0·06 |
| Cu | 30 | 990 | 9·63 | 9·93 |
| Ag | 60 | 6480 | 63·03 | 64·29 |
| Sb | 4 | 516 | 5·02 | 5·09 |
| As | 5 | 375 | 3·65 | 3·74 |
| S | 120 | 1920 | 18·67 | 17·04 |
| | | 10281 | 100·00 | 100·15 |

| | At. | | | H. Rose. *b.* | At. | | | H. Rose. *c.* |
|---|---|---|---|---|---|---|---|---|
| Zn | | | | 0·59 | | | | |
| Fe | | | | 0·33 | | | | 0·29 |
| Cu | 4 | 128 | 3·75 | 3·04 | 6 | 192 | 4·12 | 4·11 |
| Ag | 23 | 2484 | 72·78 | 72·43 | 30 | 3240 | 69·50 | 69·99 |
| Sb | | | | 0·25 | 3 | 387 | 8·30 | 8·39 |
| As | 3 | 225 | 6·59 | 6·23 | 1 | 75 | 1·61 | 1·17 |
| S | 36 | 576 | 16·88 | 16·83 | 48 | 768 | 16·47 | 16·35 |
| | | 3413 | 100·00 | 99·70 | | 4662 | 100·00 | 100·30 |

*a* is Polybasite from Durango in Mexico $= 9[(\frac{1}{3}\,Cu, \frac{2}{3}\,Ag)S] + (\frac{4}{9}\,Sb, \frac{5}{9}\,As)S^3$.—*b.* from Schemnitz $= 9[(\frac{4}{27}\,Cu, \frac{23}{27}\,Ag)S] + AsS^3$.—*c.* from Freiberg $= 9[(\frac{1}{6}\,Cu, \frac{5}{6}\,Ag)S] + (\frac{3}{4}\,Sb, \frac{1}{4}\,As)]$.—The preceding calculations show the probability of supposing that, in Polybasite, AgS and CuS replace each other, and not, as Rose is inclined to think, AgS and $Cu^2S$.

—On the specific gravity and silver-percentage of various kinds of Polybasite, *vid.* Weissenbach (*J. techn. Chem.* 10, 208.)

*b. Psaturose.*—6 AgS, $SbS^3$.—Crystalline system the right prismatic. *Fig.* 70 $u' : u = 115° 39'$; cleavage imperfect, parallel to *u* and *t*. As hard as rock-salt; very little. Spec. grav. 6·275. (H. Rose.)—Dark lead-grey inclining to iron-black; yields a black powder.—When heated in an open tube, it yields a sublimate of antimonic oxide, sometimes also of arsenious acid. On charcoal it fuses readily, and forms a white film, sometimes also emitting an odour of arsenic; when heated in the outer flame, it yields a bead of silver. Dissolves easily in hot nitric acid, with separation of sulphur and antimonic nitrate. Treated with boiling potash-ley, it turns black and gives up sulphide of antimony, which may be thrown down from the solution by acids, in the form of an orange-yellow precipitate. (Kobell.)

| | *Psaturose*, from Schemnitz. | | H. Rose. |
|---|---|---|---|
| Cu | | | 0·64 |
| 6Ag | 648 | 70·36 | 68·54 |
| Sb | 129 | 14·01 | 14·68 |
| 9S | 144 | 15·63 | 16·42 |
| | 921 | 100·00 | 100·28 |

For the percentage of silver in various kinds of Psaturose, *vid.* Weissenbach. (*J. techn. Chim.* 10, 209.)

*c. Dark Red Silver*, or *Antimonial Silver-blende.*—3 AgS, $SbS^3$.—Isomorphous with Light Red Silver, and agrees with that mineral in most of its other properties. $r^3 : r^5$ (*Fig.* 141) $= 108° 20'$. Sp. gr. from 5·7 to 5·9. Translucent; varies in colour from brown-red to dark lead-grey; yields a cochineal-coloured powder. Heated on charcoal before the blow-pipe, it decrepitates slightly; than fuses, giving off an odour of sulphurous

acid and an antimonial fume; and after long blowing in the outer flame, yields a globule of pure silver. (Berzelius.) When ignited in a stream of hydrogen gas, it yields hydrosulphuric acid, and leaves 81·48 per cent. of antimonide of silver. (Bonsdorff, *Schw.* 34, 225.) Its powder blackens in warm nitric acid, and ultimately leaves sulphur, together with antimonic nitrate. Boiling potash-ley turns it black, and extracts sulphide of antimony from it.

An *artificial Red Silver* ore, likewise yielding a red powder, is obtained by igniting sulphantimoniate of silver in a retort. (Rammelsberg.)

| | *Dark Red Silver.* | | Bonsdorff. Andreasberg. | Wöhler. Mexico. | Böttger. Mexico. | Rammelsberg. *artificial.* |
|---|---|---|---|---|---|---|
| 3Ag | 324 | 59·02 | 58·95 | 60·2 | 57·45 | 57·94 |
| Sb | 129 | 23·49 | 22·85 | 21·8 | 24·59 | 23·04 |
| 6S | 96 | 17·49 | 16·61 | 18·0 | 17·76 | 19·02 |
| Matrix | | | 0·30 | | | |
| | 549 | 100·00 | 98·71 | 100·0 | 99·80 | 100·00 |

For the percentage of silver in various kinds of dark and light red silver ore, *vid.* Weissenbach, (*J. techn. Chem.* 10, 210.)]

*d. Miargyrite.*—$AgS,SbS^3$.—Crystalline system, the oblique prismatic. Sp. gr. 5·3. Soft and easily cut; opaque; colour varying from dark lead-grey to iron-black; powder, dark cherry-red. Fuses readily when heated, and in an open tube gives off sulphurous acid, together with sublimed antimonic oxide. Heated on charcoal with carbonate of soda, it ultimately yields a globule of silver.

| | *Miargyrite.* | | | H. Rose. From Bräunsdorf. |
|---|---|---|---|---|
| Fe | | | | 0·62 |
| Cu | | | | 1·06 |
| Ag | 108 | | 35·88 | 36·40 |
| Sb | 129 | | 42·86 | 39·14 |
| 4S | 64 | | 21·26 | 21·95 |
| | 301 | | 100·00 | 99·17 |

D. Sulphantimoniate of Silver.—A solution of sulphantimoniate of sodium gradually mixed with less than an equivalent quantity of silver-nitrate, yields a brown-black precipitate, which becomes brown when dry. This precipitate dried at 130° and then ignited in a retort, gives off sulphur, together with a trace of sulphurous acid, and leaves 96·17 per cent. of artificial red silver ore. Potash-ley converts it into sulphide of silver; the yellow liquid forms with acids a copious precipitate of penta-sulphide of antimony, without evolution of sulphuretted hydrogen. (Rammelsberg, *Pogg.* 52, 18.)

The same salt, mixed however with antimonic acid, is obtained by long boiling of native sulphide of antimony with solution of silver-nitrate, in which operation it first turns brown and then black. (Rammelsberg.)

$$8SbS^5 + 15AgO = 5(3AgS,SbS^5) + 3SbO^5.$$

| | | | Rammelsberg. |
|---|---|---|---|
| 3Ag | 324 | 55·77 | 57·70 to 55·21 |
| Sb | 129 | 22·20 | |
| 8S | 128 | 22·03 | 22·85 ,, 21·88 |
| | 581 | 100·00 | |

On the other hand, if the solution of Schlippe's salt be dropped into

an excess of the silver-solution, and boiled for a while, a liquid is obtained which reddens litmus, and a black precipitate = $8AgS + SbO^5$. Boiling potash-ley extracts antimonic acid from it, and leaves sulphide of silver. At a gentle heat, it is partly converted into metallic silver; when heated to redness in close vessels, it gives off a large quantity of sulphurous acid, but no free sulphur; bakes together; yields a sublimate of antimonic oxide; and leaves a mixture of sulphide of silver, antimonic oxide, and artificial red silver ore. (Rammelsberg.)

E. Alloy of Silver, Antimony, and Potassium.—Prepared like the alloy of copper, antimony, and potassium. Steel-grey, with a strong lustre; friable; more volatile than the copper-compound; contains a very large quantity of potassium. (Serullas, *Ann. Chim. Phys.* 21, 199.)

## Silver and Tellurium.

A. Telluride of Silver.—Found native. The ore from Kolywan has the form of an obtuse rhombohedron; it is malleable, gives off an odour of horse-radish when roasted, and yields a sublimate of selenium when heated in a tube. (Hess, *Pogg.* 28, 407.) Ore from the Sawodinski mine: Coarse-grained masses, whose specific gravity varies from 8·412 to 8·565; somewhat harder than rock-salt; somewhat malleable; with a strong lustre; colour between lead-grey and steel-grey. Ignited in an open tube, it yields a white sublimate, which may partly be driven away by continued blowing, and partly contracts into fine drops. Fuses on charcoal to a black bead, which, when cold, exhibits on its surface numerous dendrites and globules of silver. Mixed with carbonate of soda, and subjected to a continued blast, it yields pure silver. In phosphorus-salt it dissolves in the inner flame, forming a clear bead, which, on cooling, becomes opalescent, or if the quantity of the mineral be considerable, assumes a yellow tint, inclining to grey. After fusion in the outer flame, the bead remains transparent and colourless on cooling. Dissolves slowly in cold, quickly in hot nitric acid; the solution, after a while, deposits tellurite of silver-oxide. (G. Rose, *Pogg.* 18, 64.) Ore from Nagyag: Exactly like that from Siberia, even in its behaviour before the blowpipe. Sp. gr. from 8·31 to 8·45. (W. Petz, *Pogg.* 57, 70.)

| | *Telluride of Silver.* | | | G. Rose. Sawodinski. | Petz. Nagyag. |
|---|---|---|---|---|---|
| Fe | | | | 0·24 to 0·50 | FePb,S, trace |
| Ag | 108 | 62·79 | | 62·42 ,, 62·32 | 61·55 |
| Au | | | | | 0·69 |
| Te | 64 | 37·21 | | 36·96 ,, 36·89 | 37·76 |
| AgTe | 172 | 100·00 | | 99·62 ,, 99·71 | 100·00 |

B. Tellurite of Silver-oxide, or Silver-tellurite.—*a. Monotellurite.*—$AgO,TeO^2$. Formed by double decomposition. Yellowish white precipitate, soluble in ammonia, on the evaporation of which a basic salt is precipitated. (Berzelius.)—*b. Bitellurite?* Separates, after a while, from the solution of native telluride of silver in nitric acid, in small acuminated square prisms, having an adamantine lustre. *Fig.* 29, $e : é$ about = 107°. Insoluble in water. Since the nitric acid solution afterwards yields crystals of silver-nitrate, the salt must contain more than 1 atom of tellurous acid to each atom of silver-oxide. (G. Rose, *Pogg.* 18, 60.)

C. Tellurate of Silver-oxide, or Silver-tellurate.—*a. Terbasic.*—1. The solution of the salt *c* in ammonia, mixed with ammonio-nitrate of silver-oxide, and evaporated, leaves a black-brown salt.—2. Bitellurate of potash added to a very dilute solution of silver-nitrate gives at first a reddish yellow precipitate, which, however, soon becomes black-brown. (Berzelius.)

| | | | | Berzelius (1). |
|---|---|---|---|---|
| $3AgO$ ..... | 348 | .... | 79·82 | ..... 79·8 |
| $TeO^3$..... | 88 | .... | 20·18 | ..... 20·2 |
| $3AgO,TeO^3$ .... | 436 | .... | 100·00 | ..... 100·0 |

*b. Sequibasic.*—$3AgO,2TeO^3$.—Remains in the form of an anhydrous, liver-coloured powder, when the salt *c* is boiled with water. (Berzelius.)

*c. Monobasic.*—$AgO,TeO^3$.—Formed by mixing concentrated solutions of silver-nitrate and monotellurate of potash. Deep yellow precipitate. When treated with water, especially at a boiling heat, it is resolved into a soluble acid salt and the insoluble terbasic salt. It dissolves in ammonia without colour. (Berzelius.)

*d. Bitellurate.*—Formed by double decomposition with concentrated solutions. Reddish yellow, bulky flakes. (Berzelius.)

*e. Quadrotellurate.*—Prepared similarly to *d.* (Berzelius.)

D. Sulphotellurite of Silver.—$3AgS,TeS^2$.—Formed by double decomposition. The black bulky precipitate, after drying, acquires metallic lustre under the burnishing steel. When distilled, it gives off sulphur, and leaves a fused, lead-grey, metallic globule, probably consisting of telluride of silver, as soft and malleable as lead, and not altered by fusion in the air. (Berzelius.)

E. Chloride of Tellurium and Silver.—Tellurium unites by fusion with chloride of silver, forming a hard white mass, which exhibits the metallic lustre and a crystalline fracture. (Berzelius.)

## Silver and Bismuth.

Silver-bismuth.—These two metals fuse easily together, and form a brittle, laminar alloy, which has the colour of bismuth; a specific gravity of 10·709 when the weights of the two metals are equal (Muschenbroek); and when heated in the air, yields metallic silver, the bismuth being converted into a vitreous oxide. An alloy of 1 pt. silver and 1 pt. bismuth does not expand in solidifying; but in the alloy of 1 pt. silver and 2 bismuth, which is steel-grey and laminar, this expansion takes place. (Marx, *Schw.* 58, 471.)

## Silver and Zinc.

Silver-zinc.—Combination takes place easily, and without incandescence. 1 pt. silver and 2 zinc form a somewhat malleable alloy, having a fine-grained fracture, and exhibiting less of a blue colour than zinc. (Gehlen.) When a solution of silver-nitrate is precipitated by zinc, an alloy is obtained which fuses with difficulty, because the oxide of zinc which is formed remains between the particles. (Fischer, *Kastn. Arch.* 13, 224.)

## Silver and Tin.

Silver-tin.—Combination takes place easily, and without incandescence. (Gehlen.) 1 pt. of silver forms a hard alloy with $\frac{1}{2}$ pt. tin; and, according to Gehlen, a malleable alloy with 2 parts of tin. The specific gravity of the compound exceeds the mean between those of its constituents; it has a granular texture, and oxidizes readily. The separation of the silver from the tin in this alloy is best effected by distilling it in the form of filings with corrosive sublimate. (Berzelius, *Lehrb.*)

B. *Stannate of Suboxide of Silver?—Silver purple.*—1. Let the three following solutions be prepared: *a.* $2\frac{1}{4}$ oz. nitric acid of specific gravity 1·1, diluted with $13\frac{1}{2}$ oz. of water; the liquid placed for 24 hours in a bottle three-fourths filled with it, and surrounded with cold water, together with half an ounce of finely-divided tin, and frequently agitated, then poured off from the tin which is not dissolved, and diluted with 16 lb. 14 oz. of water.—*β.* 30 grains of pure silver dissolved in nitric acid, the excess of acid driven off by evaporation, and the residue dissolved in 15 oz. of water.—*γ.* 180 grains of pure oil of vitriol diluted with $3\frac{3}{4}$ oz. of water. First pour *β* into *a*, stirring all the while; in a few minutes the liquid will turn yellow, then brown, then brown-red, and, lastly, dark purple-brown. As soon as the colour has ceased to become darker, add *γ*, likewise with agitation. (Without the addition of *γ*, the mixture would gradually assume a pale yellow colour, producing but a slight precipitate.) A dark purple-brown precipitate then separates, and must be washed and dried. This purple does not colour glass-fluxes. (Fricke, *Pogg.* 12, 285.) The liquid *a*, which contains nitrate of stannous oxide, may likewise be prepared by mixing protochloride of tin with a slight excess of nitrate of lead-oxide; the lead-salt which remains undecomposed renders the liquid less liable to change. (Fischer.) Solution of silver-nitrate supersaturated with ammonia, and then mixed with protochloride of tin, yields a brown-black precipitate. Silver-purple is not altered by ammonia or boiling hydrochloric acid. (Fischer, *Schw.* 56, 368.)

A bar of tin, immersed in a solution of 1 pt. nitre in 12 of water, blackens immediately, and becomes covered with a grey beard, from which white particles radiate towards the surface; these particles resemble bioxide of tin in appearance, but become darker and acquire a violet tint when exposed to sunshine. (Fechner, *Pogg.* 47, 1.)

## Silver and Lead.

A. Silver-lead.—White, lead-coloured alloy. When it is heated in the air, the lead is converted into vitreous oxide; and the other base metals united with the silver are thereby disposed to oxidate and unite with the lead-glass, and in the fused state, to soak into the porous support, the *Cupel;* this process is called *Cupellation.*—An alloy consisting of a large quantity of lead and a small quantity of silver, when slowly cooled after fusion, deposits granular crystals of lead nearly free from silver, while the alloy, richer in silver, still remains liquid. (Pattinson, *J. pr. Chem.* 10, 321.)—An alloy of silver and lead is also obtained by precipitating a solution of silver-nitrate with metallic lead. (Fisher, *Kastn. Arch.* 13, 224.)

B. Oxide of Silver and Lead.—A solution of a silver-salt mixed with excess of lead-salt, forms, with potash, a yellow precipitate, which may be freed from excess of lead-oxide by digestion in a larger quantity of potash.—The yellow precipitate blackens when exposed to light; it is resolved by ignition into lead-oxide and silver; when heated to redness in hydrogen gas, it is reduced to an easily fusible alloy of silver and lead. Dissolves readily in nitric acid, but not in potash. (Wöhler, *Pogg.* 41, 344.)

| | | | Wöhler. |
|---|---|---|---|
| 2PbO | 224 | 65·88 | 65·77 |
| AgO | 116 | 34·12 | 34·23 |
| 2PbO,AgO | 340 | 100·00 | 100·00 |

C. Sulphide of Silver and Lead.—Galena heated to whiteness with sulphide of silver in a crucible lined with charcoal, yields metallic silver and a fine-grained sulphide of silver and lead, resembling galena. (Fournet.)

D. Hyposulphite of Silver-oxide and Lead-oxide.—Aqueous hyposulphite of silver-oxide and lime forms a white precipitate with solution of lead-nitrate. (Hersche.)

E. Sulphide of Antimony, Silver, and Lead.—*Donacargyrite.*—Right rhombic prism. *Fig.* 61; $u' : u = 100°$. (Phillips.) Sp. gr. 6·194. Colour between steel-grey and blackish lead-grey. Before the blowpipe, it exhales an odour of sulphurous acid, covers the charcoal with a film of antimonic oxide and lead-oxide, and yields a globule of silver. (Hausmann & Wöhler, *Pogg.* 46, 147.)

| | *Donacargyrite.* | | Wöhler. |
|---|---|---|---|
| Fe | | | 0·11 |
| Cu | | | 1·22 |
| 3Pb | 312 | 32·43 | 30·61 |
| 2Ag | 216 | 22·45 | 22·93 |
| 2Sb | 258 | 26·82 | 27·39 |
| 11S | 176 | 18·30 | 18·74 |
| $3PbS,2AgS,2SbS^3$ | 962 | 100·00 | 101·00 |

Wöhler and Berzelius have assigned other formulæ to this mineral.

On light and dark Silver Fahl-ore, and on Silver-bismuth ore, of which new analyses are required, see Klaproth (*Beiträge*, 1, 166 and 173; 2, 291); and Fournet (*Ann. Chim. Phys.* 2, 242).

## Silver and Iron.

Silver-iron.—When these two metals are fused together, two layers are formed, the lower consisting of silver containing $\frac{1}{320}$ pt. of iron, and affected by the magnet; the upper, of iron, containing $\frac{1}{80}$ of silver, very hard, and exhibiting a denser texture than belongs to pure iron. (Morveau.) Iron may be separated from silver by fusion in the air or by cupellation, or, again, by fusion with borax and nitre, or by fusion with sulphide of lead and cupellation of the silver-lead thereby produced.

When, to a solution of silver-nitrate, slightly supersaturated with ammonia, green vitriol is added in less than the equivalent quantity, a black, granular precipitate is obtained. (If too much ammonia be added,

the precipitate is yellowish brown; too much ferrous sulphate makes it green.) Ammonia extracts from the precipitate a small quantity of silver-oxide, and colours it yellowish brown. Hydrochloric acid readily converts it into sesquichloride of iron and reddish-grey chloride of silver; and on dissolving the latter in ammonia, metallic silver remains behind. Hence it would appear that the precipitate contains oxidized iron and suboxide of silver. (Fischer, *Schw.* 56, 361.)

B. Carbide of Silver and Iron.—By fusing 500 parts of steel with 1 pt. of silver, the steel is rendered harder than the best pure steel, without bursting in forging or hardening; *Silver-steel.*—When 1 pt. of silver is fused with between 160 and 300 parts of steel, part of the silver remains uncombined, and sweats out in drops, partly in solidifying, partly in hammering; this mass is also fine-fibred and roasts easily, on account of galvanic action. (Faraday & Stodart, *Gilb.* 66, 123; further, *Ann. Chim. Phys.* 21, 64; Fischer, *Gilb.* 69, 260.)—When cast-steel is fused, first ($\alpha$) by itself in a covered crucible, and then ($\beta$), with $\frac{1}{500}$ pt. of silver, it exhibits the same properties in both cases, so that the greater goodness and density result, not from the addition of silver, but from the increased compactness resulting from the second fusion [and the addition of aluminum from the crucible ?]. Both samples exhibit the same netted appearance, and both, after hardening, have the same degree of hardness, and the same granular fracture. Specific gravity in the hardened state: of $\alpha = 7{\cdot}7647$; of $\beta = 7{\cdot}9024$; in the unhardened state: of $\alpha = 8{\cdot}0923$; of $\beta = 8{\cdot}0227$. Per centage of carbon: of $\alpha = 1{\cdot}7776$; of $\beta = 1{\cdot}6502$. (Elsner, *J. pr. Chem.* 20, 110.) The same opinion is advanced by Schauer. (*Ibid.* 20. 113.)

C. Sulphide of Silver and Iron.—*Sternbergite.*—Crystalline system, the oblique prismatic; about the shape of *Fig.* 114, but with many additional faces and without the *t*-face. Edge between *n* and *n* : edge between *u* and $u' = 119°\ 30$; cleavage distinct, parallel to *m*. Specific gravity 4·215. Somewhat harder than talc; very mild, flexible in thin laminæ. Dark pinchbeck-brown; yields a black powder. On charcoal before the blowpipe, it gives off an odour of sulphurous acid and fuses into a magnetic and generally hollow globule, having a crystalline surface covered with silver; with borax, which becomes coloured by iron, it easily yields a globule of silver. (Haidinger, *Pogg.* 11, 483.) Decomposed even by cold aqua-regia, with evolution of heat and evaporation of sulphur and chloride of silver. (Zippe, *Pogg.* 27, 690.)

| | *Sternbergite.* | | | | Zippe. |
|---|---|---|---|---|---|
| 4Fe | 112 | .... | 35·44 | .... | 36·0 |
| Ag | 108 | .... | 34·18 | .... | 33·2 |
| 6S | 96 | .... | 30·38 | .... | 30·0 |
| | 316 | .... | 100·00 | .... | 99·2 |

According to Zippe, it is $AgS,3FeS,FeS^2$. On account of the improbability of this formula, Berzelius and Rammelsberg suppose the mineral to contain one atom of sulphur more, which would give $AgS,2Fe^2S^3$.

## Silver and Nickel.

Silver-nickel.—Combination takes place with difficulty and imperfectly (Lampadius); the alloy is malleable.

### Silver and Copper.

Silver-copper.—These two metals unite in all proportions, forming a more or less reddish white, sonorous alloy, which is harder than silver, and has a density lower than the mean given by calculation.—0·8 per cent. of silver does not impair the ductility of copper at any temperature. (Karsten.)—In Germany, pure silver is called 16-*ounce* silver; that is to say, 1 ℔ avoirdupois contains 16 oz. of silver;* if the pound contains 1 oz. copper to 15 oz. silver, it is called 15-*ounce* silver; 2 copper to 14 silver, gives 14-*ounce* silver; 3 copper to 13 oz. silver, forms 13-*ounce* silver, and so on. Spoons and other articles of general use are formed of 13 and 12-ounce silver. The French silver coinage contains 9 pts. silver to 1 pt. copper.

When the alloy is simply heated in the air, only a small part of the copper oxidizes; but when a considerable quantity of lead is added, as in cupellation, the whole of the copper is oxidized. Nitric acid dissolves both the metals. Nitric acid mixed with sulphuric acid acts slowly upon copper, and serves to separate it from silver. (Grove, *Phil. Mag. J.* 15, 292; also *Pogg.* 49, 600.) An alloy containing 78 or more per cent. of silver has no action on a solution of silver-nitrate; if it contains less silver, it reduces that metal from the solution, the more quickly in proportion as the copper predominates; and not only is the excess of copper dissolved, but the reaction continues after the proportion of 78 silver to 22 copper has been reached. (Karsten, *J. pr. Chem.* 16, 379.)—[On the composition of old coins, principally consisting of copper and silver, *vid.* Walchner (*Schw.* 50, 204); Göbel (*Schw.* 60, 411); Sarzeau (*J. Pharm.* 25, 501).]

¶ A native alloy of silver and copper has been found in a mine 20 leagues east of Coquimbo in Chili. It occurs in large masses, some weighing more than a pound. The proportion of silver is variable; one sample gave 98·91 p.c. Cu and 1·09 Ag; another, which was nearly white, 92·4 Cu and 7·6 Ag. (Fr. Field, *Chem. Soc. Qu. J.* 3, 29.) ¶

B. Sulphide of Silver and Copper.—*Argentiferous Copper-glance, Stromeyerine.*—Crystalline system the right prismatic. *Fig.* 56, with the *p*-face. The angles of the lateral edges differ but little from those of a regular six-sided prism; $i : t$ and $a : u = 116°$ *nearly;* it has, therefore, the same crystalline form as Copper-glance. (G. Rose, *Pogg.* 28, 427.) Sp. gr. 6·255; very brittle, with a conchoidal fracture. Colour between dark lead-grey and iron-black, with a strong lustre. (Hausmann & Stromeyer, *Schw.* 19, 325.)—Fuses readily before the blowpipe, diffusing an odour of sulphurous acid, but no fumes, and forming a grey, semi-malleable globule, having the metallic lustre. Colours fluxes by the copper which it contains. Yields a large silver button when cupelled with lead. (Berzelius.) Dissolves in nitric acid, with separation of sulphur.

| | *Argentiferous Copper-glance.* | | | | Stromeyer. Schlangenberg. | | Th. Sander. Rudolstadt. |
|---|---|---|---|---|---|---|---|
| Fe | | | | | 0·33 | | 0·24 |
| 2Cu | 64 | | 31·37 | | 30·48 | | 30·95 |
| Ag | 108 | | 52·94 | | 52·27 | | 52·71 |
| 2S | 32 | | 15·69 | | 15·78 | | 15·92 |
| $Cu^2S, AgS$ | 204 | | 100·00 | | 98·86 | | 99·82 |

* According to the German weights, 1 mark or half a pound, contains 16 *loth* of silver, a *loth* being equal to half an ounce.

C. Selenide of Silver and Copper.—*Eukairite.*—Soft, slightly ductile, with a fine-grained fracture; lead-grey, yielding a shining streak and a grey powder.—Heated in an open tube, it yields selenium and selenious acid. Heated on charcoal before the blowpipe, it fuses, emitting a strong odour of selenium, and yields a grey, soft, but brittle metallic globule. When cupelled with lead, it yields a large quantity of silver. Colours fluxes like copper. With hot nitric acid, it forms a solution from which water throws down selenite of silver-oxide. (Berzelius, *Schw.* 23, 477.)

| *Eukairite.* | | | | Berzelius. From Skrickerume. |
|---|---|---|---|---|
| 2Cu | 64 | 25·40 | | 23·05 |
| Ag | 108 | 42·85 | | 38·93 |
| 2Se | 80 | 31·75 | | 26·00 |
| Earthy matter | | | | 8·90 |
| $Cu^2Se, AgSe$ | 252 | 100·00 | | 96·88 |

## Silver and Mercury.

A. Silver-amalgam.—Found native.—*Formation.*—1. A bar of silver, immersed in mercury at the ordinary temperature, takes up a small quantity of mercury in the course of 24 hours, but remains malleable; even in six weeks, the combination is of very inconsiderable amount; but if the mercury be heated to the boiling point and gradually cooled, soft needles of amalgam are deposited on the bar at the surface of the mercury. (Daniell.)—2. The amalgam is quickly formed when a thin red-hot silver-leaf, or silver precipitated in the pulverulent form, is thrown into heated mercury.—3. When a solution of silver in nitric acid is reduced by mercury, the precipitated silver unites with a portion of the mercury in the form of a crystalline amalgam: *Silver-tree, Arbor Dianæ.* —If the quantity of mercury be too large, the amalgam formed is liquid instead of crystalline; to prevent this, it is recommended to use a compound of mercury with $\frac{1}{8}$ silver instead of pure mercury; according to Proust, however, pure mercury acts quite as well. A small quantity of free acid in the silver-solution accelerates the precipitation; moreover, the solution must not be too concentrated.—When sodium-amalgam [in excess?] is introduced into a strong silver-solution, a soft amalgam of silver is formed. (Böttger.)—Klaproth introduces an amalgam of 8 pts. mercury and 1 pt. silver, into a solution of 1 pt. of silver in nitric acid, after diluting it with 24 parts of water. Vitalis (*Ann. Chim.* 72, 93) hangs a lawn bag full of mercury in a solution containing both silver and mercury; removes the bag with the adhering crystals from the liquid at the end of the precipitation; and hangs it up in an empty glass. Berzelius recommends the introduction of an amalgam of 7 pts. mercury and 1 pt. of silver into a mixture of 3 pts. of a saturated silver-solution and 2 pts. of a saturated mercury-solution.—When mercury is left for a considerable time at the bottom of a tolerably dilute solution of silver, the silver-tree first formed sometimes disappears again, being dissolved by the liquid amalgam below it; and then, after a while, long four-sided prisms are produced, which have a strong lustre, are soft and easily pulverized, and contain 31·7 per cent. of mercury with 68·3 silver, and therefore consist of $Hg^4Ag^2$. (Hünefeld, *Schw.* 61, 125.)—A silver-tree analyzed by Dehne (*Crell. Chem. J.* 1, 54) contained, on the contrary, 81·36 per cent. mercury, and 18·64 silver.

Prepared by (2): silver-white, granular, soft mass, which grates between the fingers; by (1) and (3): crystallizes in long, shining prisms, growing to one another. — At a red heat, it evolves mercury; but, according to Gay-Lussac (*Ann. Chim. Phys.* 58, 218), silver may retain a small quantity of mercury, even at the melting-point. If the amalgam be very carefully heated, the silver remains in an arborescent form. (Schlosser, *Crell. n. Chem. J.* 6, 91.) Hence the application of the amalgam to the process of *silvering at a high temperature*.

*Native amalgam.*—*a. Arquerite.*—$HgAg^6$.—From Arqueros in Chili. (Domeyko & Berthier, *Compt. rend.* 14, 567; also *J. pr. Chem.* 26, 360.)

| | | *Arquerite.* | | Domeyko. |
|---|---|---|---|---|
| Hg | 100 | 13·37 | | 13·5 |
| $6Ag$ | 648 | 86·63 | | 86·5 |
| $Hg,Ag^6$ | 748 | 100·00 | | 100·0 |

*b. Amalgam* of Mineralogists.—$Hg^2Ag$ and $Hg^3Ag$.—Belongs to the regular system. *Figs.* 2, 3, 6, and other forms. Sp. gr. from 13·7 to 14·1. Harder than calcspar; slightly brittle; silver-white.

| | | | Klaproth. Moschellandsberg. |
|---|---|---|---|
| $2Hg$ | 200 | 64·93 | 64 |
| Ag | 108 | 35·07 | 36 |
| $Hg^2,Ag$ | 308 | 100·00 | 100 |

| | | | Heyer. Moschellandsberg. | | Cordier. Allemont. |
|---|---|---|---|---|---|
| $3Hg$ | 300 | 73·53 | 73·3 | | 72·5 |
| Ag | 108 | 26·47 | 25·0 | | 27·5 |
| $Hg^3Ag$ | 408 | 100·00 | 98·3 | | 100·0 |

B. Nitrate of Silver-oxide and Mercuric-oxide.—$HgO,NO^5 + AgO,NO^5$.—Prismatic crystals, which readily dissolve in water without decomposing. (Berzelius, *Lehrbuch.*)

C. Nitrate of Mercuric Oxide with Iodide of Silver.—$2AgI + 2(HgO,NO^5) + Aq$.—Crystallizes from a solution of iodide of silver in hot aqueous mercuric nitrate, of sp. gr. 1·35, in fine needles, which cause the liquid to assume a solid consistence; they are decomposed by water. (Preuss, *Ann. Pharm.* 29, 328.)

## Other Compounds of Silver.

With Gold, Platinum, Palladium, Rhodium, and Iridium.

## Chapter XXXVIII.

# GOLD.

Wilh. Lewis. *Physik. chem. Abhandl.* Berl. 1764. B. 1, S. 62 to 424.
Hatchett.—Alloys of Gold. *A. Gehl.* 4, 50.
Proust. *J. Phys.* 62, 131; also *N. Gehl.* 1, 477.
Oberkampf. *Ann. Chim.* 80, 140.
Vauquelin. *Ann. Chim.* 77, 321; also *Schw.* 3, 323.
Berzelius.—Oxides of Gold. *Schw.* 7, 43. Further: *Ann. Chim. Phys.* 18, 146; also *Schw.* 34, 81. Sulphomolybdate of Gold. *Pogg.* 7, 277 and 288. Sulpharseniate of Gold. *Pogg.* 7, 30 and 150. Chloride of Gold and Potassium. *N. Ed. J. of Sc.* 3, 288.
J. Pelletier.—Facts relating to the history of Gold. *Ann. Chim. Phys.* 15, 5 and 113; also *Schw.* 31, 305; also *N. Tr.* 5, 2, 168.
Figuier.—Chloride of Gold and Sodium. *J. Pharm.* 6, 64; also *Repert.* 10, 169. *J. Pharm.* 8, 137; also *Schw.* 35, 342; also *N. Tr.* 6, 2, 301. Oxides of Gold and Fulminating Gold. *Compt. rend.* 18, 813.
Bonsdorff.—Chlorine- and Bromine-salts of Gold. *Pogg.* 17, 261; 33, 64.
Johnston.—Chlorine-salts of Gold. *N. Edinb. J. of Sc.* 3, 131 and 290. Iodide of Gold. *Phil. Mag. J.* 9, 266.
Fordos & Gehlis.—On the action of Terchloride of Gold on Hyposulphite of Soda. *N. Ann. Chim. Phys.* 13, 384; abst. *Ann. Pharm.* 56, 252.
Himly.—On two new series of double salts, containing Protoxide of Gold. *Ann. Pharm.* 59, 95.
Yorke.—On the Aurosulphurets of Sodium and Potassium. *Chem. Soc. Qu. J.* 1, 236.
Frémy.—Chemical Researches on Gold. *N. Ann. Chim. Phys.* 31, 478; also *Ann. Pharm.* 79, 40.

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Synonymes: *Aurum*, *Sol*, *Or*.

*History.* Gold has been known from the earliest times; the *Electrum* of the ancients consisted of gold and silver. Vitruvius and Pliny describe the amalgamation of gold. The alchemists, Basil Valentine for instance, were acquainted with the solution of chloride of gold, and with fulminating gold; the latter compound has been more exactly investigated by Scheele, Bergman, Berzelius, and Dumas. Andreas Cassius and his son, in 1685, described the preparation of *gold-purple*, which was then adapted by Kunkel to the preparation of red glass, and afterwards examined in a variety of ways. Proust and Oberkampf discovered the teroxide of gold, and examined many of the chemical characters of its hydrochloric acid solution; the latter also discovered sulphide of gold. Berzelius discovered the protoxide and protochloride; Pelletier the proto-iodide, and the mode of preparing the pure teroxide; Johnston the teriodide; Balard the bromide. Besides the chloride of gold and potassium discovered by Javal,

and the chloride of gold and sodium discovered by Figuier, several other corresponding salts have been made known by Bonsdorff and Johnston. Hatchett has examined several alloys of gold.

*Sources.* Gold is almost always found native; it occurs in large quantities, and in many places; it is sometimes found in combination with silver (in Electrum); with tellurium (in Native Tellurium); with silver and tellurium (in Graphic and Yellow Tellurium); and with lead and tellurium (in Foliated Tellurium). It sometimes occurs in small quantity in metallic sulphides, as in galena, iron pyrites and copper pyrites. A native amalgam of gold has been found in Columbia, and an alloy of gold and bismuth in Rutherford county in North America. (*Jahresber. L. & K.* I. 1153.)

*Preparation.* 1. From gold-ore, which has been tolerably well freed by mechanical means from matrix or river-sand, the gold may be obtained by simple fusion with borax, or other substances adapted to bring the adhering earthy matters into the liquid state.—2. Poorer gold ores are either fused with lead, in a similar manner to silver-ores, or directly treated with mercury, after which the lead or mercury is separated in the manner already described in the case of silver.

If by these various modes of preparation, an alloy of gold and silver is obtained, the separation of these metals may be effected in the following ways: 1. *Fusion with Sulphur.* The granulated alloy is fused with 0·3 pt. sulphur, which combines with the silver, and forms a liquid sulphide, while the finely-divided gold remains suspended in it; a small quantity of litharge is then added, which gives rise to the formation of sulphurous acid and sulphide of lead, and again separates a portion of the silver, which then combines with the gold, forming an alloy, richer in the latter metal. This alloy sinks to the bottom of the crucible, and, after cooling, is separated by the hammer from the superposed sulphide of silver and lead (the *Plachmal*). This substance, when fused with the addition of a small quantity of litharge, yields silver, which, for the most part, still contains a little gold. When the *Plachmal* has thus been completely exhausted of gold, it is generally cupelled with lead, to obtain the silver. This mode of separation is adopted with alloys which contain but very little gold. The resulting alloy is often treated repeatedly with sulphur in the same manner, till the proportion of gold is raised to one-fourth, after which the treatment with nitric acid is usually adopted.—2. *Fusion with Sulphide of Antimony.* The alloy is mixed with twice its weight of sulphide of antimony, and fused, with constant stirring, in a crucible previously glazed with borax; if the amount of silver in the alloy exceeds one-third, a proportional quantity of sulphur is added to the mixture. Sulphide of silver is then formed, and the gold combines with the antimony, forming a lower stratum of alloy, which is afterwards freed from antimony by ignition in the air, or by fusion with nitre. As the sulphide of silver thus formed still contains gold, it is again twice fused with sulphide of antimony, whereby an additional quantity of antimonide of gold is obtained. The whole amount of antimonide of gold thus produced is again fused with twice its weight of sulphide of antimony, then freed from antimony, either by fusing it alone, while air is blown upon it, or by fusion with three times its weight of nitre, and sometimes finally melted into a mass by heating it with $\frac{3}{4}$ pt. borax, $\frac{1}{4}$ nitre, and $\frac{1}{4}$ glass.—3. *Separation by Cementation.* The granulated alloy is arranged

in alternate layers, with a mixture of 2 parts of brick-dust and 1 part of common salt, in porous crucibles, which are exposed for a period varying from 24 to 36 hours, to a low red heat. Under these circumstances, the aqueous vapour from the wood fire penetrates the crucibles, and acts upon the mixture in such a manner as to separate hydrochloric acid, which then forms chloride of silver, with evolution of hydrogen; and the chloride of silver, together with the common salt, sinks into the brick-dust (p. 162). The gold obtained by this process is, after washing, from 21 to 22 carats fine; from the remaining mass, the silver is obtained by amalgamation. This process is employed in America. (Boussingault.) A mixture of 4 pts. brick-dust, 1 pt. common salt, and 1 pt. calcined green vitriol, may also be used as a cement.—4. *Separation by Sulphuric acid.* The granulated alloy, in which the gold should not amount to quite one-half, but the silver may be in considerable excess, is heated in a platinum or cast-iron vessel, with oil of vitriol, the quantity of which amounts to 3 parts for every 4 parts of silver to be dissolved, the heat being continued as long as sulphurous acid is evolved; and the resulting silver-sulphate is separated from the gold-powder by boiling water. To free the gold still further from silver, it is again heated for three hours in the platinum vessel, with a small quantity of oil of vitriol. After this treatment, the gold retains only $\frac{1}{3}$ per cent. of silver. The silver-solution is warmed in leaden vessels, with metallic copper immersed in it, whereby the silver is separated, and blue vitriol obtained. (Sobolewsky, *Ann. Pharm.* 24, 94; J. C. Jordan, *J. pr. Chem.* 9, 49.)—¶ This process has lately been made the subject of an elaborate investigation by Pettenkofer (*Dingl. Pol. J.* 104, 118; abstr. *Jahresber. L. & K.* 1, 1027; further, *Dingl. pol. J.* 111, 357; *Jahresber.* 2, 635), of which the following are the principal results. The gold obtained by the first operation contains small quantities of lead-sulphate, basic ferric sulphate, and traces of sulphide of copper, which may be removed by digestion with carbonate of soda, washing, and subsequent treatment with nitric acid. The residue contains, on the average, 97 per cent. of gold, 2·8 of silver, and 0·2 of platinum. The silver is contained in it in the state of regulus, and cannot be dissolved out, either by boiling sulphuric or by boiling nitric acid. After digestion in solution of sesquichloride of iron, not a trace of chloride of silver is dissolved out by ammonia. The gold thus purified may also be heated several times in contact with sulphur, till all the sulphur is volatilized, without giving rise to the formation of sulphide of silver. When it is treated with boiling sulphuric acid, to which pounded bichromate of potash is added, chromic oxide is formed, the gold is rapidly dissolved, while the silver and platinum remain unaltered. The only reagents capable of dissolving out the residual portion of silver from the refined gold, are the alkaline bisulphates, the soda-salt being the most eligible on account of its cheapness. The best mode of proceeding is to mix the gold with one-fourth of its weight of Glauber's salt in an iron vessel, pour in another equivalent of oil of vitriol (0·7 of the weight of the neutral sulphate), and heat the mixture till the salt becomes liquid. Sulphate of silver-oxide is then formed, with evolution of sulphurous acid (and of hydrochloric acid, from the common salt contained in the Glauber's salt), and the excess of sulphuric acid likewise escapes; the mass has a great tendency to cake together, which must be prevented by stirring. The greater part of the sulphate becomes reduced to the neutral state, and to dissolve out the rest of the silver, it is merely necessary to repeat the process once, heating the mixture, however, only till about half the sulphate has become neutral. To

separate the gold from the resulting mass, it must be boiled with sulphuric acid in the ordinary way, whereby the sulphates of soda and silver-oxide are dissolved; the residue is then washed, dried, and fused with nitre. The first fusion yields refined gold, containing 994 parts of pure gold in 1000; and the second, from 998 to 999 parts, or not more than 0·1 or 0·2 per cent. of silver. The facility and success of the operation depend greatly upon the proportion of Glauber's salt and upon the temperature, which should be kept a little below redness.—The presence of platinum in refined gold explains the well-known fact that this metal never exhibits a proper degree of fineness and softness, until it has been fused with nitre, platinum being easily oxidized by fusion with that substance. A portion of gold likewise passes into the slag together with the platinum; for although gold is not oxidized, or but very slightly, when fused alone with nitre, it is nevertheless acted on with great facility when platinum is likewise present. A small portion of platinum, amounting to 1 or 2 parts in a thousand, escapes oxidation, and remains in the refined gold. The slag which remains after the fusion leaves, when treated with water, a soft grey powder, containing alumina, silica, and lime (from the crucibles) —potash,—certain insoluble metallic compounds formed during the treatment with sulphuric acid, viz., lead-sulphate, basic ferric sulphate, and sulphide of copper,—the oxides of gold, platinum, palladium, and osmium, formed by the action of the nitre,—and finally a small quantity of metallic gold. Formerly this powder was merely levigated with water to separate the metallic gold, and the remainder was thrown away. But Pettenkofer has shown that this rejected matter contains 19 or 20 per cent. of gold, from 2·5 to 3·5 per cent. of platinum, and a small quantity of silver. The lightness of the residue had caused the presence of these metals to be overlooked, and prevented their separation by the amalgamation process. Pettenkofer, however, has devised a method by which the gold and platinum may be profitably separated. The slags collected from several operations are soaked in water, and left to stand for 8 or 12 days, till they are reduced to a fine soft paste, which is then mixed with 2 parts of litharge, 1 part of tartar, 4 of dry carbonate of soda, and 2 of pounded glass, these proportions being calculated for 8 parts of the dry slag. The mixture is thoroughly dried in a copper or iron vessel; then thrown, by small portions at a time, into a red-hot crucible; and exposed to a gradually increasing heat, till it is brought to a state of tranquil fusion. If the process has been allowed time enough, a sharply separated regulus of lead is found, after cooling, at the bottom of the greyish slag. This lead is then cupelled, and the resulting button of metal is granulated and dissolved in aqua-regia in a retort, to which a receiver is adapted, because the vapours carry small portions of gold and platinum along with them. The heat is continued till all the nitric acid is driven off, the remaining solution filtered from the insoluble residue (AgCl and PbCl), put into a porcelain dish, and precipitated while still warm with green vitriol. The gold which falls down in lumps, is separated by decantation, washed, and fused with $\frac{1}{32}$ of its weight of nitre, to remove a trace of palladium: the product is fine gold. The solution poured off from the gold is precipitated with metallic iron, the precipitate (chiefly consisting of platinum) boiled with nitric acid, then dissolved in aqua-regia, and precipitated as chloroplatinate of ammonium. An attempt to disintegrate the slags with sulphuric acid, led to difficulties insuperable in practice. ¶

5. *Separation by Nitric acid; Separation by Quartation.*—The granulated alloy, which must contain at least 3 pts. of silver to 1 of gold.

is first treated with cold weak nitric acid, and afterwards with strong acid at a boiling heat; the gold-powder is then separated from the silver-nitrate by washing with hot water, and afterwards fused with borax and nitre. The gold, after this treatment, retains but a mere trace of silver. ¶ According to Pettenkofer (*Jahresber.* 1, 1030), the proportion of 3 parts silver to 1 gold is not absolutely necessary in this process, the separation taking place quite sharply when the quantity of silver added does not exceed 1·75 pt. Moreover, gold refined by quartation retains a larger quantity of silver, the more the proportion of the latter metal is increased beyond the limit above mentioned. ¶—6. *Separation by Aqua-regia.*—The granulated alloy, very rich in gold, is resolved by repeated treatment with nitric acid, into chloride of gold which dissolves, and chloride of silver which remains undissolved, and must be washed. The gold solution is freed by evaporation from the nitric acid still present, then diluted with water, and mixed with green vitriol, whereby the gold is precipitated in the form of a brown powder, which must be fused with a small quantity of borax and nitre.—Pure gold is also obtained on the small scale by solution in aqua-regia, precipitation with green vitriol, digestion of the precipitate with hydrochloric acid, washing, and fusion with borax.

The Kremnitz ducats contain in 24 carats, 23 carats 9 grains of gold, and therefore only 3 grains of foreign metal; the Dutch ducats contain 23 carats 7 grains of gold. (1 carat=12 grains.)

Gold is obtained in the pulverulent state by precipitating aqueous chloride of gold with green vitriol and other reducing agents; and according to the nature of the precipitant, and the mode of conducting the process, the powder exhibits various degrees of fineness, and is consequently more or less adapted for gilding on porcelain, &c. The powder formed by pouring the gold-solution into the green vitriol is softer than when the contrary method is adopted, in which case it is more laminar and shining. (Otto, *Ann. Pharm.* 26, 86.) A peculiarly fine gold powder is obtained by pouring the gold-solution, at 100°, into a solution of mercurous nitrate; also by precipitating the gold-solution with hydrochlorate of terchloride of antimony.—¶ According to C. T. Jackson (*Sill. J.* [2], 6, 187), gold is obtained in the form of a soft, yellow, spongy mass, by adding to a concentrated gold-solution, a small quantity of oxalic acid, then a sufficient quantity of carbonate of potash to dissolve nearly all the gold in the form of aurate of potash, then a large quantity of crystallized oxalic acid, and finally heating the liquid rapidly to the boiling point. ¶

*Properties.* Gold crystallizes, both naturally and artificially, in crystals belonging to the regular system. Native gold exhibits the forms of *Fig.* 1, 2, 3, 4, 5, 6, 8, 9, and 11. (Hauy, G. Rose, *Pogg.* 23, 196; Neumann, *Pogg.* 24, 384.) Gold is softer and less tenacious than silver; not very elastic; becomes somewhat harder by hammering. It is the most ductile of all metals; and may be hammered out into leaves only $\frac{1}{282000}$ of an inch thick; *Gold-leaf.* One grain of gold yields a leaf having a surface of 56·75 square inches, and the same quantity may be drawn out into a wire 500 feet long. Specific gravity of fused gold 19·2; of hammered gold, from 19·3 to 19·4. ¶ According to G. Rose (*Pogg.* 73, 1; 75, 403), gold, after fusion *per se*, has a specific gravity varying from 19·30 to 19·34; after fusion under carbonate of soda, from 19·32 to 19·33; under borax, from 19·33 to 19·34; under

chloride of sodium, 19·30 (the determinations were made at 17·5 C.); after pressure under the die, from 19·31 to 19·34. Finely-divided gold precipitated by green vitriol was found to vary in density from 19·55 to 20·72; and when precipitated by oxalic acid, its density was 19·49. ¶—In the coherent state, gold has the reddish yellow colour and lustre exhibited by ducat-gold; in the pulverulent state, it is brown and dull, but acquires the metallic lustre by pressure. Very finely divided gold diffused through a watery liquid appears blue, by transmitted light; leaf-gold, sometimes blue, sometimes green. The coloured transparency of gold first becomes apparent when the thickness is reduced to $\frac{1}{2000}$ of a line. (Ehrenberg, *Pogg*, 24, 40.)—Pulverulent gold may be welded and rolled into leaf in the same manner as platinum, by Wollaston's process. (Fournet, *Ann. Chim. Phys.* 75, 435.)—Gold melts, with considerable expansion, at 1200° C. (Pouillet), at 1381° C. (Guyton-Morveau), at 1421° C. (Daniell); it is therefore less fusible than silver or copper; in the fused state, it exhibits a bluish green colour.—It exhibits a scarcely perceptible volatility at the strongest heat of a blast-furnace, in the focus of a burning mirror, and in a flame fed with oxygen gas. A plate of silver held over gold strongly heated in the focus of a burning mirror becomes slowly gilded. (Homberg.)

*Atomic weight of Gold;* 196·71 (Berzelius, *Pogg.* 65, 319); 196·3 (Levol, *N. Ann. Chim. Phys.* 30, 355).

## *Compounds of Gold.*

### Gold and Oxygen.

### A. Protoxide of Gold, or Aurous Oxide. AuO.

*Suboxide of Gold, Gold-suboxydul, Protoxyde d'Or.*—1. Formed by precipitating protochloride of gold with cold, dilute potash. (Berzelius.) The protoxide thus obtained is contaminated with a large quantity of metal. (Figuier.)—2. By precipitating aqueous terchloride of gold with mercurous nitrate. (Figuier.) [The reaction is probably as follows:

$$AuCl^3 + 2(Hg^2O, NO^5) = AuO + 3HgCl + HgO, 2NO^5.$$

An excess of mercurous nitrate must be avoided, as it would occasion the precipitation of calomel.]—The protoxide of gold is also produced by boiling the teroxide or terchloride for a long time with solution of caustic potash or soda—by boiling the aqueous solution of the terchloride with carbonate of potash or soda—by boiling the teroxide with acetic acid—or by mixing the terchloride with excess of potash, and then boiling it with tartrate, citrate, or acetate of potash, or with other vegetable and animal matters. (Figuier.)

Dark green powder. (Berzelius.) Blackish violet when moist, bluish violet when dry. (Figuier.)

| | | | | | Berzelius. |
|---|---|---|---|---|---|
| Au ..... | 199 | .... | 96·14 | ..... | 96·13 |
| O ..... | 8 | .... | 3·86 | ..... | 3·87 |
| AuO ..... | 207 | .... | 100·00 | ..... | 100·00 |

($Au^2O$ = 2 . 1243·013 + 100 = 2586·026. Berzelius.)

When immersed for some hours in caustic potash, it is completely

resolved into a dark brown mixture of auric oxide and metallic gold, which gilds the vessel. (Berzelius.) Permanent at ordinary temperatures, decomposes at 250°. (Figuier.)—Hydrochloric acid immediately converts it into metallic gold and an aqueous solution of the terchloride. (Berzelius, Figuier.)—Does not combine with acids; slightly soluble in caustic potash. (Berzelius.) Combines with acids as well as with alkalis. (Figuier.)—It is clear that the oxides examined by Figuier and by Berzelius were not the same; and as the former has given no analysis of his oxide, his statements are comparatively questionable.

Purple oxide of Gold.—*Formation.* 1. By the combustion of gold. A gold wire, through which the charge of a powerful electric battery is passed, burns with a green light, and is converted into vapour, which deposits itself on the adjacent surfaces in the form of gold-purple. —This purple oxide is formed even in air 200 times rarefied; but in a perfect vacuum, the gold is scattered about in fine metallic globules. (Guyton-Morveau.) A piece of gold-leaf burns with a green light in the circuit of the voltaic battery. Thomson burned gold-wire in an ignited jet of hydrogen and oxygen gases. Gold placed in the focus of a Tschirnhausen's burning mirror, imparts a red colour to the surface of the glazed support.

The presence of other bodies favours the oxidation of gold at high temperatures, by predisposing affinity, the oxide formed being generally red. When gold-leaf is triturated with various substances and exposed to the blowpipe-flame on a small cupel, the following results are obtained: With potassium: The alloy oxidizes quickly as it forms, and is converted into a black powder, which fuses into a violet glass with silica and borax. Hydrate and carbonate of potash do not act upon the gold, but sink into the cupel.—With hydrate or nitrate of baryta: The gold disappears and colours the baryta red-brown.—With nitrate of strontia: The gold disappears and colours the strontia bluish, with red spots here and there.—With hydrate of lime: The lime acquires a reddish or a bluish-grey colour. When gold-leaf is placed in a crucible with hydrate of lime in alternate layers, and ignited, the gold disappears, and the lime acquires a flesh-colour.—With moistened magnesia: Lavender-blue, infusible powder, the gold disappearing.—The compounds thus obtained with baryta, strontia, lime, or magnesia, yield a sky-blue or violet glass with borax.—When gold-leaf is triturated with silk-paper and the paper burnt, a metallic ash is left, which, if moistened with a solution of potash, soda, baryta, or strontia, and again ignited, sometimes but rarely exhibits traces of metal.—With silica containing potash: Red colouring, accompanied by disappearance of the gold.—With chromic oxide: The gold disappears slowly and the mass remains green.—With carbonate of manganous oxide, or peroxide of manganese: The gold disappears slowly.—With uranic oxide: The gold acquires a brown tarnish and disappears in the dirty green uranoso-uranic oxide.—With antimony: The antimony disappears in fumes and the gold is left behind.—With antimonious acid: The gold remains, but imparts a reddish colour to the acid.—With zinc: Grey powder, the gold disappearing.—With oxide of zinc: The gold disappears slowly and yields a grey powder.—With tin or stannic oxide: First an alloy, then a grey powder.—With iron-filings: The gold disappears quickly and yields a grey mass; and if this substance be ignited with fresh gold-leaf, as long as the latter disappears, a red mass is obtained, still having the form of the filings, and very slightly soluble in

dilute sulphuric acid, the solution not being attended with evolution of gas.—With ferroso-ferric oxide: The gold disappears much more slowly. —With hydrated oxide of cobalt: The gold becomes dull and of a copper colour, but does not disappear completely.—With hydrated oxide of nickel: The gold becomes bluish grey, and soon disappears completely.—With copper-filings: The gold remains unaltered.—Most of the compounds obtained with the heavier metallic oxides yield up the gold in the metallic state when fused with borax, the other oxide remaining dissolved in the borax. (J. A. Buchner, *Repert.* 29, 1.)

2. A neutral or acid gold-solution treated with various deoxidizing agents, sometimes only with the aid of light or heat, yields a purple-red body, which is either the purple oxide alone, or a compound of that oxide with the unaltered or altered precipitant; see the reactions of aqueous terchloride of gold.

It is in this red form that gold enters into glass-fluxes.

Proust, Buisson, Figuier, and others, regard the purple body as very finely-divided gold, the division being favoured by the presence of foreign bodies. On the whole, however, it is more probable, as Berzelius supposes, that this red or purple substance contains oxygen. But whether the red oxide be intermediate in composition between the protoxide and teroxide, or identical with the protoxide—to which, at all events, Figuier ascribes a similar violet colour—is a question which remains to be decided by future experiments.

### B. Teroxide of Gold, Auric Oxide, or Auric Acid. $AuO^3$.

*Goldoxyd, Peroxyde d'or, Acide aurique.—Formation:* Water, and the greater number of acids, sulphuric acid, for example, exert no oxidizing action upon gold. The metal is, however, converted into teroxide, and in that form dissolved, by chlorine-water, by fuming nitric acid, and by nitric or chromic-acid in union with hydrochloric acid; it is also slightly oxidized by red-hot nitre.

*Preparation.* 1. By precipitating a hot aqueous solution of terchloride of gold, free from excess of hydrochloric acid, with a strong excess of potash. (Oberkampf.) This precipitate is small in quantity, and contains potash. (Pelletier.)—2. By exactly saturating the same solution with carbonate of soda, and boiling as long as a precipitate is formed. To separate the rest of the oxide from the filtrate, and thereby decolorize the liquid completely, it must be supersaturated with carbonate of soda, and then neutralized while hot with sulphuric acid. (Figuier.)—¶ 2′. By mixing an aqueous solution of terchloride of gold (freed as far as possible from excess of acid by repeated evaporation and re-solution) with caustic potash, till the liquid becomes strongly alkaline; adding chloride of barium, till the precipitate, which is yellow at first, begins to be whitish; decomposing the precipitate, which consists of aurate of baryta, by boiling it for a few minutes with dilute nitric acid; and, lastly, washing the auric oxide thoroughly, and drying it in the dark. (Figuier, *N. J. Pharm.* 12, 401.) ¶—3. By precipitating the same solution at a boiling heat with baryta-water, collecting the precipitate of aurate of baryta, and digesting it in nitric acid, to dissolve out the baryta. (Dumas.) It is difficult to extract the whole of the baryta. (Pelletier.)—4. By heating the same solution with excess of magnesia or zinc-oxide, and dissolving out the

magnesia or zinc-oxide which has combined with the separated auric oxide, by strong nitric acid. (Pelletier.)—¶ 4. By adding to the solution of chloride of gold a sufficient quantity of potash to redissolve the precipitate first produced, boiling for a quarter of an hour, whereupon the liquid, which is at first dark brown, gradually assumes a yellow tint—then adding sulphuric acid in slight excess—collecting the resulting precipitate on a filter, and washing it with water, till the wash-water no longer gives a precipitate with baryta-salts. The precipitate consists of teroxide of gold or auric acid. The first addition of the potash converts the chloride of gold into an oxychloride, which then forms a soluble compound with the potash; and if the solution be treated with an acid without previous boiling, a precipitate is obtained consisting of the oxychloride, which may be distinguished from the teroxide by dissolving slowly, but completely, in pure water. It is only by continued boiling that the compound of the oxychloride with potash is converted into the aurate of potash, the conversion being attended with the change of colour above noticed. The auric acid obtained in the manner just described is not quite free from potash, even after long-continued washing. It may be purified completely by treating it with very strong nitric acid, which dissolves it readily—mixing the solution with water, which immediately precipitates the auric acid—and washing the precipitate thoroughly with pure water. (Frémy, *N. Ann. Chim. Phys.* 31, 478; also *Ann. Pharm.* 79, 40.) ¶

*Properties.* Brown-black powder, or brown mass, having a conchoidal fracture.

| | | | Berzelius. | Javal. | Oberkampf. | Richter. | Proust. |
|---|---|---|---|---|---|---|---|
| Au ..... | 199 | 89·24 | 89·225 | 89 35 | 90·9 | 79·71 | 92·1 |
| 3O ..... | 24 | 10·76 | 10·775 | 10·65 | 9·1 | 20·29 | 7·9 |
| $AuO^3$ .... | 223 | 100·00 | 100·000 | 100·00 | 100·0 | 100·00 | 100·0 |

($Au^2O^3 = 2 . 1243·013 + 300 = 2786·026$. Berzelius.)

Decomposed by light, or at an incipient red heat, into metallic gold and oxygen gas. Gives up its oxygen to vegetable acids and many other substances. When boiled with potash-ley, it is resolved into protoxide of gold and aurate of potash. (Figuier.) ¶ Decomposed by hydriodic acid, vapours of iodine being evolved, and metallic gold precipitated. Hydrochloric and hydrobromic acids dissolve it without decomposition. (Frémy.) ¶

*Combinations.* *a.* With Water.—Hydrated Auric Oxide.—1. Obtained by mixing a solution of terchloride of gold, not containing free acid, with a quantity of potash only just sufficient to neutralize the hydrochloric acid, and repeatedly washing the reddish yellow precipitate—which does not appear till after the lapse of several hours—first with boiling water, and afterwards with dilute nitric acid, to dissolve out the adhering potash and chloride of gold. (Pelletier.)—2. By proceeding as in the second method for the preparation of the anhydrous oxide, but washing the precipitate with dilute instead of concentrated nitric acid. (Pelletier.) The hydrate, after drying in the air, which takes place but slowly, exhibits a chesnut-brown colour. When heated to 100°, or when treated with aqueous potash, it gives up its water, and is converted, with diminution of volume, into the black oxide, part of which, however, is reduced to the metallic state. By digestion with alcoholic potash, it is reduced to very hard, shining gold scales (used in miniature-painting). Perfectly soluble in hydrochloric acid. (Pelletier.)

The yellow precipitate obtained by Oberkampf, on mixing an aqueous neutral solution of terchloride of gold with less than an equivalent quantity of a fixed alkali, and regarded as *basic hydrochlorate of auric oxide*, or as *basic hydrochlorate of auric oxide and potash*, inasmuch as it gave up hydrochloric acid to caustic potash, and was thereby converted into the black oxide, is, according to Pelletier, the hydrate of auric oxide contaminated with a small quantity of terchloride of gold, which may be removed by boiling water and by nitric acid.

Identical with this, appears to be the precipitate which Vauquelin obtained, by heating the acid gold-solution with pure potash or carbonate of potash. This precipitate, when recently formed, was of loose texture and reddish yellow colour; resembled dried blood, when deprived of moisture; had a rough metallic taste; and excited a flow of saliva. When digested in water, it gave up a small quantity of auric oxide, precipitable by green vitriol, the portions first dissolved, but not the subsequent portions, being accompanied by a small quantity of hydrochloric acid (according to Pelletier, a small quantity of adhering aurate of potash dissolved in the water); it likewise dissolved in excess of caustic potash, but not in carbonate of potash, leaving, however, a brown or blue powder [metallic gold?].

*b.* With Acids, it forms the salts of Auric Oxide, or Auric Salts.—The affinity of auric oxide for the greater number of acids is but slight: thus, it does not combine with carbonic, boracic, or phosphoric acid, and dissolves only in very great excess of strong sulphuric or nitric acid, forming solutions in which it is very loosely combined; it is likewise scarcely possible to form compounds of this oxide with vegetable acids, inasmuch as those acids reduce it with facility. The auric salts at present known are yellow, with a tinge of red; have a rough and caustic taste, and exert a poisonous action. When heated, they leave metallic gold, which is also thrown down from their solutions by most metals, by green vitriol, &c. [For the other reactions, vid. *Aqueous Terchloride of Gold.*]

*c.* With the alkalis, and some of the earths, forming compounds called *Aurates.*

### C. *Perauric Acid.* $AuO^5$?

*Goldsäure, Acide peraurique.*—When auric oxide is boiled for a long time with aqueous potash, aurous oxide is precipitated, without evolution of gas, and a solution is formed containing peraurate of potash and a small quantity of aurate,—which, on the addition of sulphuric or nitric acid, yields a precipitate of auric oxide, accompanied at first by an evolution of carbonic acid gas, but not of oxygen. The liquid, quickly filtered from this precipitate, exhibits a bright yellow colour at first; but at the temperature of 60° or 65°, it is decomposed in a few seconds, becoming green and turbid, giving off a few gas-bubbles, and depositing metallic gold.—If a neutral solution of chloride of gold be boiled with excess of potash till a considerable quantity of protoxide has separated from it, and then mixed, first with chloride of barium, and then with baryta-water, a yellow precipitate is first thrown down, and afterwards a greenish one; and on decomposing this precipitate with sulphuric acid, auric oxide remains, mixed with sulphate of baryta, and the liquid contains perauric acid. According to this, 2 At. $AuO^3$ are resolved by boiling with potash

into 1 At. AuO, and 1 At. $AuO^5$. (Figuier.)—¶ According to Frémy, the black precipitate formed by boiling a solution of terchloride of gold with potash—the precipitation always taking place at the moment when the change of colour occurs (p. 208)—consists of metallic gold; and its formation arises, either from the accidental presence of organic substances, or more generally from the decomposition of a certain quantity of protochloride of gold, which is mixed with the terchloride, and is converted by the action of the alkali into metallic gold and aurate of potash. ¶

## Gold and Phosphorus.

Phosphide of Gold.—*a.* By fusing gold with glacial phosphoric acid and charcoal powder, a pale yellow, friable mass is obtained, having a granular fracture and containing 4 parts of phosphorus to 100 of gold. (Pelletier.)

*b.* By heating finely-divided gold with phosphorus in a sealed glass tube exhausted of air, Edmund Davy obtained a grey, metallic-looking mass, containing 14 p. c. (1 At.) of phosphorus, which volatilized at a gentle heat.

When phosphuretted hydrogen gas in excess is passed through an aqueous solution of terchloride of gold, a black precipitate is formed which exhibits no metallic aspect, and does not yield gold by elutriation.—It does not fume in the air, and appears to undergo no alteration by exposure; when it is heated in contact with air, the phosphorus burns away; aqua-regia converts it into terchloride of gold and phosphoric acid; it decomposes the terchloride of gold just as phosphorus does. (Oberkampf.) —According to H. Rose (*Pogg.* 14, 184), the precipitate formed by phospuretted hydrogen gas consists of metallic gold.

## Gold and Sulphur.

A. Protosulphide of Gold.—Formed by passing sulphuretted hydrogen gas through a boiling solution of chloride of gold. Part of the sulphur is thereby converted into sulphuric acid, and a black-brown powder is precipitated, exhibiting a deep-yellow streak, and containing 92·97 pts. gold to 7·03 sulphur. (Berzelius.)—According to Levol, the precipitate formed by sulphuretted hydrogen and a boiling solution of terchloride of gold, consists, not of sulphide, but of metallic gold.

B. Tersulphide of Gold.—Gold does not unite with sulphur by fusion.—*Preparation.* 1. By precipitating a solution of terchloride of gold with sulphuretted hydrogen or an alkaline hydrosulphate at ordinary temperatures.—Black precipitate.—According to Levol (*N. Ann. Chim. Phys.* 30, 355), the precipitate thus formed consists of $AuS^2$, which contains water, and does not give it up till heated to 140°.—2. By fusing gold in excess with pentasulphide of potassium, dissolving the fused mass in water, and precipitating by an acid. The sulphide of gold then falls down in deep yellow flakes, which turn brown on drying. (Berzelius.)

| | | | | | Oberkampf. | | Fellenberg. | | Bucholz. |
|---|---|---|---|---|---|---|---|---|---|
| Au..... | 199 | .... | 80·57 | ..... | 80·39 | .... | 81·48 | .... | 82 |
| 3S..... | 48 | .... | 19·43 | ..... | 19·61 | .... | 18·52 | .... | 18 |
| $AuS^3$.... | 247 | .... | 100·00 | ..... | 100·00 | .... | 100·00 | .... | 100 |

At a very gentle heat, the sulphur volatilizes and metallic gold remains. (Oberkampf.)—When moderately heated in a current of chlorine gas, it is converted into chloride of sulphur and metallic gold. (Fellenberg, *Pogg.* 50, 71.)—If left for two days in the excess of gold-solution from which it has been precipitated, it is converted into gold and sulphuric acid. (Jacquelain, *Compt. rend.* 14, 642.)—Dissolves in aqueous sulphide of potassium, forming sulphide of gold and potassium. In aqueous potash, it dissolves partially (forming sulphide of gold and potassium and hyposulphite of potash: *Berzelius*), while metallic gold remains. (Oberkampf.) —According to Oberkampf, the elements of this compound cannot be separated by elutriation, so that the precipitate cannot, as Proust maintains, be regarded as a mere mixture of gold and sulphur.

C. Sulphate of Auric Oxide, or Auric Sulphate.—Auric oxide dissolves sparingly in cold oil of vitriol.—Yellow, strongly acid liquid, which, when gently heated, or when mixed with water, deposits metallic gold. (Pelletier.)

D. Sulphocarbonate of Gold.—$AuS^3,3CS^2$.—Solution of chloride of gold, mixed with aqueous sulphocarbonate of calcium, yields a turbid mixture, which slowly becomes clear, and deposits a greyish-brown precipitate, black after drying; this precipitate, when subjected to distillation, gives off sulphur, and leaves gold blackened by charcoal. (Berzelius.)

Gold does not unite with selenium when the two are heated together.

## Gold and Iodine.

A. Proto-iodide of Gold, or Aurous Iodide.—Iodine exerts a scarcely perceptible action on gold; hydriodic acid, none whatever.—*Preparation.* 1. By the action of hydriodic acid on teroxide of gold, water being formed at the same time, and $\frac{2}{3}$ of the iodine set free. (Pelletier.)

$$AuO^3 + 3HI = AuI + 3HO + 2I.$$

2. By precipitating a neutral solution of chloride of gold with aqueous iodide of potassium added in proper proportion. In this case, also, $\frac{2}{3}$ of the iodine is set free, and is expelled by heating the mixture. (Pelletier.)

$$AuCl^3 + 3KI = AuI + 3KCl + 2I.$$

Aqueous iodide of potassium is added in small portions, stirring each time, to the neutral gold-solution, as long as a precipitate is thereby produced. As the point of complete precipitation is approached, the liquid acquires a reddish colour, and then the iodide of potassium must be added only by drops; an excess would re-dissolve a portion of the precipitate, producing a dark-coloured solution. Hence it is necessary to hit the exact proportion. (Instead of iodide of potassium, hydriodic acid or aqueous iodide of iron may be used; the latter, when newly prepared, has the advantage over iodide of potassium, that compound often containing free alkali; in using the iodide of iron, however, it is likewise necessary to avoid adding it in excess, which would re-dissolve the precipitate.) The precipitate is washed with water by repeated subsidence and decantation, till all the chloride of potassium is dissolved out; it is then thrown upon a filter; the filter, after the water has run off, spread out on a piece of paper; and the precipitate freed from adhering iodine

by three or four days' drying in a hot-air chamber at a temperature between 30° and 36°, the surface of the precipitate being renewed twice a day. At that temperature, only the free iodine is given off, the combined portion not escaping in any length of time. If, on the contrary, an attempt be made to remove the free iodine by boiling the precipitate with water, or by continued washing with alcohol, part of the aurous iodide is decomposed, so that free gold becomes mixed with the precipitate; hence it must only be washed for a short time with alcohol, and afterwards with water. (Fordos, *J. Pharm.* 27, 653; also *Repert.* 75, 344.)—If the gold-solution be mixed with a slight excess of iodide of potassium and heated, the greenish yellow precipitate diminishes in quantity; and, as the liquid cools, small, shining, golden yellow crystalline scales make their appearance, similar to those of iodide of lead, but containing only from 33·96 to 34·43 per cent. of iodide, because the precipitate which separates at the beginning of the action, and mixes with the crystals, is nearly pure gold containing only 0·1 per cent. of iodine. (Johnston.)—When the gold-solution is in excess, a bluish green mixture of iodine and protiodide of gold is obtained [after the removal of the free iodine?], containing 34·93 per cent. of iodine. (Johnston.)—Iodide of gold, nearly white and semi-crystalline, may likewise be obtained by cautiously adding neutral hydriodate of ammonia to a moderately dilute and perfectly normal solution of chloride of gold, adding one measure of alcohol to 3 measures of the mixture, decanting after a few hours, and freeing the black precipitate from adhering iodine by washing with alcohol. (Meillet, *J. Pharm.* 27, 665.) —3. By pouring aqueous iodide of potassium on protochloride of gold, washing the precipitate on a filter, and drying it in cold air. (Johnston.) —4. By boiling very finely divided gold with aqueous hydriodic acid, with frequent addition of a small quantity of nitric acid, which, however, must not be added in such proportion as to decompose the whole of the hydriodic acid,—and filtering the resulting solution of iodide of gold in aqueous hydriodic acid while still hot. Part of the aurous iodide then separates, on cooling, in the form of a lemon-yellow, crystalline powder; another portion, in the form of a greyish yellow powder, on boiling the remaining liquid with nitric acid till the hydriodic acid is completely decomposed, the precipitated iodine being afterwards expelled by long boiling. (Pelletier.)—Fordos thinks it preferable to let the iodine evaporate in the hot-air chamber, as above described.

*Properties.* Lemon-yellow, shining, crystalline powder (greenish yellow when precipitated, according to method (4), by hydrochloric acid). (Pelletier.) When prepared by (3) it is a pale green powder. (Johnston.) A greenish yellow colour generally indicates the presence of free gold. (Fordos.) Obtained, according to method (2), by crystallization from a hot liquid, it forms shining, golden yellow scales. (Johnston.) Inodorous; tasteless at first, but if kept for some time on the tongue, it excites a peculiar taste by decomposing the saliva.

| | | | | Fordos. | Johnston. | Pelletier. |
|---|---|---|---|---|---|---|
| Au..... | 199 | 61·23 | ..... | 61·13 | 61·15 | 66 |
| I ..... | 126 | 38·77 | ..... | 38·87 | 38·85 | 34 |
| AuI .... | 325 | 100·00 | ..... | 100·00 | 100·00 | 100 |

Fordos examined the compound prepared by (2), after 14 days' drying over lime in a vessel not exhausted of air.—Johnston examined the pale green powder obtained by (3), which, according to his analysis, does not

contain any free gold, notwithstanding its green colour.—Pelletier's iodide of gold was prepared by (4), and undoubtedly contained metallic gold.

*Decompositions.* Protiodide of gold kept for some time in a bottle at ordinary temperatures, continually acquires a darker, dingy, greenish yellow colour, and gilds the sides of the vessel, iodine being at the same time evolved and destroying the cork. In a drying chamber, at temperatures between 30° and 35°, it remains unaltered for a considerable time; between 50° and 60° it decomposes more quickly, becoming covered in a few days with metallic gold. Heated to 70° in a current of dry air, it becomes covered with a golden film, even in three hours; at 120°, it is immediately and completely decomposed into metallic gold and iodine vapour. (Fordos.)—The crystalline scales obtained, according to (2), from the hot solution, give off 9 per cent. of iodine when exposed to the air for 10 days at ordinary temperatures; at 66°, they give off a small quantity of iodine; at 110°, nearly all; and at 204°, the last portions. (Johnston.)—Water, sulphuric acid, and nitric acid, which have no action on this compound in the cold, decompose it at a boiling heat into iodine-vapour and gold; this decomposition is entirely due to the heat. (Pelletier, Fordos.)—Hydrochloric acid exhibits a red colouring even at 70°. (Fordos.)—Bromine decomposes protiodide of gold immediately, and forms with water an orange-yellow solution, probably consisting of terbromide of gold. (Fordos.)—Chlorine gas (but not chlorine-water) produces instant decomposition, and if a little water be present, forms a solution of terchloride of gold. (Fordos.)—Iodine in presence of water, forms aqueous iodide of iron and metallic gold. (Fordos.)—Potash-ley immediately separates the gold, forming iodide of potassium and iodate of potash. (Pelletier, Fordos.)—Many organic compounds likewise separate the gold. The action of alcohol does not begin for several hours, is slower the more dilute the alcohol, and continues for several days. Fat triturated with iodide of gold exerts a decomposing action in a day; saliva is gradually coloured brownish violet by it; sugar forms with it a yellow mixture, which soon acquires a dingy yellow colour. Gum, on the contrary, impedes the spontaneous decomposition of iodide of gold. (Fordos.)—Aqueous hydriodic acid forms the red-brown solution C, with separation of about two-thirds of the gold. In a similar manner, aqueous iodide of potassium or iodide of iron separates two-thirds of the gold, a compound of teriodide of gold with the more basic metallic iodide being formed at the same time. Aqueous sal-ammoniac and common salt act but slightly, even at 35°. (Fordos.)

B. Teriodide of Gold, or Auric Iodide.—When a normal solution of terchloride of gold is gradually added to aqueous iodide of potassium, the liquid gradually acquires a dark green colour, and yields a dark green precipitate of $AuI^3$, which redissolves on agitation. A portion of gold, however, is very apt to remain undissolved, while the liquid retains free iodine; for, in consequence of the easy decomposibility of the $AuI^3$, a small quantity of AuI is precipitated, and when it is redissolved by the iodide of potassium, metallic gold separates out. After 1 atom of terchloride of gold has been added to 4 At. iodide of potassium, a further addition of the gold-solution decolorizes the liquid, and forms a permanent dark green precipitate of teriodide of gold, because the teriodide of gold and potassium at first produced is thereby decomposed :

$$4KI + AuCl^3 = 3KCl + KI,AuI^3;$$

Further: $$3(KI,AuI^3) + AuCl^3 = 3KCl + 4AuI^3.$$

The precipitate may be washed without any considerable decomposition taking place; but in drying it gives off a large portion of its iodine. Exposed to the air at ordinary temperatures, it is gradually converted into yellow protiodide of gold, and afterwards into pure gold. Teriodide of gold is likewise decomposed by alkalis and earths.—It combines with aqueous hydriodic acid, and with the more basic metallic iodides, forming with the latter a series of very dark-coloured iodine-salts. (Johnston, *Phil. Mag. J.* 9, 266.)

| | | | |
|---|---|---|---|
| Au | 199 | | 34·49 |
| 3I | 378 | | 65·51 |
| $AuI^3$ | 577 | | 100·00 |

C. Aqueous Hydriodate of Auric Iodide, or Acid Hydriodate of Auric Oxide.—1. Formed by dissolving finely-divided gold in aqueous hydriodic acid mixed with iodine. (Pelletier.)—2. By dissolving teriodide of gold in aqueous hydriodic acid. (Johnston.)—3. By dissolving protiodide of gold in aqueous hydriodic acid, the action being attended with separation of metallic gold. (Fordos.)—The dark brown solution, when left to evaporate freely, deposits small black prisms, which, on exposure to the air, acquire a fine purple colour, probably from separation of iodine. (Johnston.) Whether the prisms consist of teriodide of gold, or of the hydriodate of that compound, is a question not yet examined.—Fordos likewise obtained a few needles on evaporating the solution in the hot-air chamber.—Ammonia added to the solution throws down a detonating compound. (vid. *Gold and Nitrogen.*)

D. Iodate of Auric Oxide, or Auric Iodate.—Iodic acid and iodate of potash form with aqueous terchloride of gold, a yellow precipitate, soluble in a large quantity of water. (Pleischl.)

## Gold and Bromine.

Terbromide of Gold, or Auric Bromide.—Gold dissolves slowly in bromine-water, forming a liquid which imparts a violet colour to animal substances, and, on evaporation, leaves yellow bromide of gold, which is resolved by heat into bromine-vapour and metallic gold. (Balard.)—The gold is abundantly dissolved, forming a red solution, and on evaporation, there remains greyish black bromide of gold, which, when ignited, leaves 50 per cent. of gold. Bromide of gold dissolves readily in water, forming a deep scarlet liquid, which exhibits the reactions of a solution of chloride of gold, and yields scarlet crystals. One part of these crystals imparts a perceptible colour to 5000 parts of water. (Lampadius, *Schw.* 50, 377.)—Hydrobromic acid forms with solution of chloride of gold a dark red mixture of aqueous bromide of gold and free hydrochloric acid; the latter may be distilled off, and the bromide of gold may be dissolved out of the mixture by ether. (Wilson, *Athenæum*, 1839, 674; abstr. *Jahresber.* 20, 108.)—Bromide of gold combines with the more basic metallic bromides, forming salts, which Bonsdorff calls *Bromo-aurates.*

## Gold and Chlorine.

A. Protochloride of Gold, or Aurous Chloride.—Formed by heating terchloride of gold to the melting point of tin, in a porcelain basin placed on the sand-bath, stirring constantly, and continuing the heat till no more chlorine is evolved.—Yellowish-white. (Berzelius.)

| *Calculation*, according to Berzelius. | | | |
|---|---|---|---|
| Au | 199·0 | .... | 84·9 |
| Cl | 35·4 | .... | 15·1 |
| AuCl | 234·4 | .... | 100·0 |

At a somewhat higher temperature, it is resolved into gold and chlorine gas; by water it is resolved into terchloride of gold, which dissolves, and metallic gold, the decomposition being very quickly produced by boiling water; it takes place slowly in the dark, more quickly on exposure to light, and almost instantly on boiling.—Aqueous solution of potash converts the compound into protoxide of gold and aqueous chloride of potassium. (Berzelius.)

Hydrogen gas, passed for some time through a neutral solution of chloride of gold, gives it a fine purple-red colour, without forming a precipitate. The liquid, after long standing, deposits a small portion of gold, and when heated, is immediately converted, with deposition of metallic gold, into the yellow solution of chloride of gold. (Oberkampf.) Buisson, on passing hydrogen gas through the gold-solution, obtained a brown precipitate. Proust and Schweigger-Seidel (*Schw.* 65, 268) obtained neither reddening nor precipitation. In an experiment, also, made by the author with pure hydrogen gas, in daylight, a small quantity of gold was precipitated, but no change of colour occurred in the liquid.

B. Terchloride of Gold, or Auric Chloride.—Gold-leaf heated in chlorine gas absorbs it without visible combustion.—Gold-leaves and finely-divided gold obtained by precipitation dissolve [when the air has access?] in heated hydrochloric acid. (Proust.)—Gold dissolves, even at ordinary temperatures, in chlorine-water, in mixtures of nitric acid with hydrochloric acid, sal-ammoniac, and common salt, and in mixtures of hydrochloric acid with nitrates or with chromic acid. Formula for solution of gold in aqua-regia, supposing aqueous chloride of gold to be formed:

$$Au + NO^5 + 3HCl = AuCl^3 + 3HO + NO^2;$$

or supposing ter-hydrochlorate of auric oxide to be produced:

$$Au + NO^5 + 3HCl = AuO^3,3HCl + NO^2.$$

The solution in aqua-regia, which may contain a considerable quantity of free hydrochloric and nitric acid—the *acid solution of chloride of gold*—gives off these acids, together with water, when evaporated to dryness at a temperature somewhat above 100°; the residual terchloride of gold is, however, mixed with a small quantity of unevaporated free acid and protochloride of gold, which remains undissolved when the residue is treated with water. (Berzelius.) A small quantity of protochloride of gold may be produced, even if the evaporation be not carried quite to dryness; for the separation of chlorine from the terchloride takes place almost as readily as the evaporation of the free acid. (Berzelius.)

Dark ruby-red or red-brown mass, which becomes darker whenever it is heated. (Berzelius.)

| | *Calculation*, | according to Berzelius. | |
|---|---|---|---|
| Au ..... | 199·0 | .... | 65·20 |
| 3Cl ..... | 106·2 | .... | 34·80 |
| $AuCl^3$ ..... | 305·2 | .... | 100·00 |

Gives off 2 atoms of chlorine at a temperature much below redness, leaving protochloride of gold, which, by exposure to a stronger heat, is converted into spongy gold. It is soluble in water; forms, with the more basic metallic chlorides, reddish yellow chlorine-salts, which Bonsdorff calls *Chloro-aurates;* it is likewise soluble in alcohol, ether, and volatile oils, which, however, exert a reducing action upon it.

*Aqueous Terchloride of Gold*, or *Ter-hydrochlorate of Auric Oxide.—Normal Solution of Chloride of Gold.*—This is the aqueous solution of pure terchloride of gold, and therefore contains no free hydrochloric (or nitric) acid. As terchloride of gold obtained by evaporation generally contains a little free acid, a perfectly normal solution of the terchloride can only be obtained by boiling the protochloride with water. (Berzelius.) The solution is brown-red when concentrated, reddish yellow when dilute. It reddens litmus.

C. Hydrochlorate of Auric Chloride.—The solution of gold in aqua-regia, prepared with an excess of gold and hydrochloric acid, so that all the nitric acid is decomposed, solidifies on evaporation and cooling, in a crystalline mass made up of laminæ, and having a bitter, rough, but non-metallic taste. (Proust.) It yields long, light yellow, four-sided prisms and truncated octohedrons. (Thomson, *System.*) The crystals fuse when heated, give off hydrochloric acid and chlorine, and leave a mixture of terchloride and protochloride of gold. (Berzelius.) They deliquesce in the air (Proust), but are not quite so soluble in water as terchloride of gold. (Berzelius.) When a solution of gold in aqua-regia is evaporated over the water-bath for a day, it remains liquid while hot, but solidifies in a crystalline mass on cooling.

*Acid solution of Chloride of Gold.—Ordinary Gold-solution.*—The reddish yellow, normal solution immediately acquires a paler yellow colour on the addition of hydrochloric acid. (Berzelius.) The acid solution is obtained in the purest state by dissolving the above-mentioned crystals in water; and, mixed with excess of hydrochloric acid, by heating an excess of gold with aqua-regia, adding hydrochloric acid as long as nitrous fumes are evolved. Without this precaution, undecomposed nitric acid would likewise remain mixed with it. When a mixture of hydrochloric acid and nitre is used, the liquid also contains chloride of potassium; and if nitric acid be used with sal-ammoniac or common salt, the solution will contain nitrate of ammonia or nitrate of soda. The aqueous solution of common salt, nitre, and alum, also dissolves gold; this was the *Menstruum sine strepitu* of the ancients.—The solution is of a lemon-yellow colour, inclining to orange-yellow; it tastes rough and bitter, and under the action of light, imparts a purple-red colour to the skin.

The following are the reactions of the *Normal* and *Acid Gold-solutions:* In those cases in which observers have not specified the exact nature of the solution employed, we shall denote it by the simple term, *Gold-solution.*

Many substances throw down metallic gold or the purple oxide from these solutions. The normal solution, in a very dilute state, when kept

for three years in a stoppered bottle in the shade, deposits a large quantity of delicate gold spangles. (Basseyre, *Ann. Chim. Phys.* 54, 46.) The acid solution remains unaltered under similar circumstances. The normal solution, left to evaporate in the air, deposits a small quantity of gold on the sides of the vessel; also when kept in a vessel filled with nitrogen gas. Hence the nitrogen exerts a reducing action. (Fischer, *Pogg.* 17, 137.)—Hydrogen gas passed through the normal solution colours it red. (Oberkampf; *comp.* p. 215.)—Phosphorus immersed either in the normal or in the acid solution, quickly throws down the gold in the form of a yellow, ductile film, which envelopes the phosphorus.—Hyphophosphorous acid (Dulong) and phosphorous acid quickly precipitate gold from either solution in the form of a metallic powder. Characters traced on paper with a solution of gold become metallic when immersed in a vessel containing air and phosphorus. (H. Rose, *Pogg.* 14, 184.)—According to Oberkampf, phosphuretted hydrogen gas colours the solution first brown, then purple, and precipitates metallic gold, with formation of phosphoric acid; if, however, the phosphuretted hydrogen is in excess, phosphide of gold is likewise precipitated.—According to H. Rose, on the contrary, no phosphide is thrown down.—Sulphur has no action on gold-solution at ordinary temperatures; in a hot solution it becomes penetrated by veins of gold. (Fischer, *Pogg.* 12, 505.)—Sulphurous acid and alkaline sulphites immediately reduce the gold-solution at ordinary temperatures, causing it to appear bluish by transmitted light; on boiling, the gold separates in the form of a brown powder. (Berthier, *N. Ann. Chim. Phys.* 7, 82.) The sulphurous acid is converted into sulphuric. (Jacquelain.) The reduction takes place, even in very dilute solutions, but not when a large excess of hydrochloric acid is present, even if the acid be partly neutralized by ammonia. (Wackenroder, *J. pr. Chem.* 18, 295.)—Selenium acts only on a hot solution, and acquires a deposit of gold, which prevents further action. (Fischer.)—Nitric oxide gas and the vapour of fuming nitric acid reduce gold both from the normal and from the acid solution. Each bubble of gas becomes enveloped in gold, and in a short time the whole of the metal is precipitated. (Fischer, *Pogg.* 17, 480.)—Most of the base metals, and likewise mercury, silver, palladium, and platinum, precipitate the gold, sometimes in the metallic state, as a brown powder or a gilding deposit, sometimes in the form of gold-purple, which appears to be a compound of the purple oxide of gold (p. 206) with the oxide of the other metal.—*Manganese* reduces gold but very slightly from its solutions. (Fischer.) [On account of the carbon which it contains?]—*Arsenic* rapidly precipitates the gold in the metallic state. (Fischer.) It forms a purple. (Lesage.)—*Antimony*, which acts very slowly, becomes gilt, when immersed in a gold solution. (Fischer.) It produces a purple. (Lesage.)—*Tellurium* becomes covered with a film of gold which stops the further action, even when heat is applied. (Fischer, *Pogg.* 12, 503.)—*Bismuth* precipitates the gold completely in a few hours, and becomes gilded. (Fischer, *Pogg.* 9, 255.) It yields a purple. (Lesage.)—*Zinc* throws down the gold quickly and completely in the form of a brown powder. (Fischer.)—*Cadmium* slowly precipitates the gold in the form of a brown powder. (Fischer.)—*Tin* quickly throws down metallic gold at first, afterwards the purple of Cassius. (Fischer.)—*Lead* causes rapid metallic precipitation in dendrites. (Fischer.)—*Iron* and *Cobalt* precipitate the gold quickly and completely in the form of a brown powder. (Fischer.)—*Nickel* acts in the same manner, but more slowly. (Fischer.)—*Copper* precipitates the gold quickly and completely,

in the form of a brown powder. (Fischer.)—*Mercury* slowly takes up the gold, and forms an amalgam. (Fischer.)—*Silver* produces a slow precipitation of the gold. (Fischer, *Pogg.* 2, 255.) It forms a purple. (Thomson, *System.*)—*Platinum* reduces gold from the neutral solution, and from that of the chloride of gold and sodium, but not from the acid gold-solution. *Platinum* retains this property after boiling with hydrochloric, nitric, or nitro-hydrochloric acid, but not after boiling with oil of vitriol. (Fischer, *Pogg.* 16, 124.)—*Palladium* precipitates gold completely. (Fischer, *Pogg.* 10, 607.)—Titanium, tungsten, molybdenum, and chromium exert no reducing action on gold-solutions. (Fischer, *Pogg.* 16, 127.)—For practical observations on the gilding of metals by precipitation, *vid.* Barnal, *N. Ann. Chim. Phys.* 18; also *J. pr. Chem.* 39, 116; abstr. *Ann. Pharm.* 60, 219.

Arseniuretted hydrogen and antimoniuretted hydrogen gases precipitate gold from the solution, the former with formation of arsenious acid. (Soubeiran, Jacquelain.)—Arsenious acid dissolved in hydrochloric acid, precipitates gold slowly at ordinary, quickly at higher temperatures. (Levol.)—Terchloride of antimony precipitates gold completely from very dilute solutions, in the form of a very beautiful, dull gold-coloured powder, but from stronger solutions, in an arborescent form:

$$3SbCl^3 + 2AuCl^3 = 3SbCl^5 + 2Au.$$

The pentachloride of antimony, as it forms, is decomposed by the water, yielding hydrochloric and antimonic acids, which may mix with the gold. The latter must therefore be dissolved in a mixture of a little nitric with a large quantity of hydrochloric acid, so that all the nitric acid may be decomposed, (otherwise a fresh quantity of antimonic acid would be formed,) and the excess of hydrochloric acid may retain the antimonic acid in solution. The solution of antimonious acid in hydrochloric acid does not reduce gold. (Levol, *Ann. Chim. Phys.* 76, 505; also *J. pr. Chem.* 24, 253.) The chloride of antimony must be added in the state of a very acid solution.—Ferrous salts, green vitriol, for instance, added to either the normal or the acid gold-solution, precipitate the gold in the form of a soft brown powder, which colours the liquid brown by reflected light, and blue by transmitted light, provided the solution be diluted to a certain extent:

$$AuCl^3 + 6(FeO,SO^3) = Au + 2(Fe^2O^3,3SO^3) + Fe^2Cl^3.$$

A solution of chloride of gold containing only 1 part of gold in 40,000 parts of liquid still appears brown by reflected and blue by transmitted light, on the addition of green vitriol; if the proportion of liquid amounts to 80,000 parts, a sky-blue colour is produced; with 160,000 parts, pale violet, even by reflected light; with 320,000 parts, very pale violet; and with 640,000 parts, scarcely perceptible violet. (Lassaigne, *J. Chim. méd.* 8, 586.)—The precipitation of gold by green vitriol is complete, even from a very dilute solution; addition of hydrochloric acid accelerates the action, and heat causes the gold to unite in laminæ. (Morin.)—Aqueous protochloride of tin added to a concentrated gold-solution, either normal or acid, throws down brown pulverulent gold-tin; from a dilute solution it precipitates the purple of Cassius (vid. *Purple of Cassius*). A solution of chloride of gold containing 1 pt. of gold in 10,000 of liquid gives with protochloride of tin, a red precipitate; with 20,000 to 40,000 of liquid, a wine-red colouring; with 80,000, a brown-red colouring; with 160,000 to 320,000, pale brown; and with 640,000, a scarcely perceptible colouring.—A mixture of chloride of gold with hydrochlorate of pentachloride of antimony or terchloride of bismuth, forms a purple precipitate, not

only with protochloride of tin, but likewise with green vitriol or mercurous nitrate. (Buisson, *J. Pharm.* 16, 638, and 641.) On the other hand, Desmarest (*J. Pharm.* 17, 219), by mixing a solution of chloride of gold with acid hydrochlorate of antimonic oxide or solution of bismuth-nitrate, and then with a dilute solution of green vitriol, obtained merely a precipitate of metallic gold, but no purple.—A solution of dichloride of copper in hydrochloric acid precipitates gold from both the normal and the acid solution (Proust); so likewise does the solution of dibromide of copper in hydrobromic acid. (Löwig.)—Mercurous nitrate produces thick, dark blue flakes, which, on heating the mixture, are converted into a blue-black gold powder. The precipitate formed in an acid solution at ordinary temperatures, is violet, and contains gold, mercury, and chlorine. (Proust.) According to Fischer (*Schw.* 56, 363), it is bluish grey, and consists of a compound of mercuric oxide with red oxide of gold. According to Figuier, it consists of violet protoxide of gold.—If the two solutions are acid and concentrated, and prepared in definite proportions, the gold is precipitated in the form of a soft powder adapted for painting on porcelain.

Many organic compounds added to gold-solutions throw down either metallic gold or the red oxide, which then unites with the organic compound more or less decomposed, and forms a red precipitate. The simplest mode of viewing these decompositions is to regard the chloride of gold as hydrochlorate of auric oxide, the oxygen of which is transferred, wholly or partially, to the carbon and hydrogen of the organic compound, forming carbonic acid and water.—Oxalic acid added either to a normal or to an acid gold-solution, throws down all the gold in the metallic state, with evolution of carbonic acid, the action taking place slowly in the dark, more quickly when the mixture is exposed to light. (Pelletier.) The mixture immediately becomes brown by reflected, and green by transmitted light, and in 24 hours deposits all the gold in metallic laminæ. (G. Rose, *Pogg.* 23, 170.) The gold-solution dropped on crystallized oxalic acid, or oxalate of ammonia, produces a bright red colouring in the course of 15 hours. Berzelius could not produce this red colouring in any way whatever. (*Jahresber.* 11, 179.) In sunshine, or with the aid of heat, oxalic and citric acid may produce purple precipitates. (Desmarest.)—Formic acid and formiate of potash precipitate the dilute solution but imperfectly, and even when the liquid is boiled with a large quantity of the potash-salt, one-third of the gold remains in solution. (Marin, *J. Pharm.* 26, 104.)—Tartrate, citrate, and acetate of potash, precipitate metallic gold from the solution, without formation of carbonic acid. (Pelletier.) Tartrate of soda does not precipitate the gold till the liquid is heated, but then the precipitation takes place suddenly. (R. Phillips, *Phil. Mag. J.* 2, 95.) Hydrochloric acid in excess retards or prevents the precipitation by these vegetable acids.—Pyroracemic acid precipitates the gold completely, and with metallic lustre, on the application of heat. (Berzelius, *Pogg.* 36, 29.)—Gallic acid immediately precipitates metallic gold from the dilute acid solution, producing first a yellowish, and then a brown colouring. Tincture of galls colours the solution first brown, then purple-red, and afterwards throws down metallic gold. (Pfaff, *Analyt. Chem.*) Ether, volatile oils, and recently ignited charcoal, separate the gold only in sunshine, or at 109°. (Rumford, *Scher. J.* 2, 3.) The former gild the sides of the vessels; the charcoal becomes spotted with gold.—Sugar, manna, gum, the juices of fruit, and the decoctions of catechu, sumach, turmeric, fustic, grains of Avignon, Brazil-wood, cochineal, anise, and gamboge, form red pulverulent precipitates with the gold-solution. (Proust, *Scher. J.*

10, 95.) The gold-solution, boiled with sugar, yields first a light red, and afterwards a dark red precipitate. With glycerine, at a temperature somewhat below 100°, it immediately forms a violet powder. (A. Vogel.) A solution of 1 part of terchloride of gold in 30 parts of water, mixed with alcohol, sugar-solution, or starch-solution (the latter formed by boiling), deposits metallic gold, slowly in the dark, but in the course of a few hours, when exposed to light, so that it appears brown by reflected, and blue by transmitted light. (Fischer, *Kastn. Arch.* 9, 349.)—Linen, silk, wool, epidermis, and ivory, saturated with the gold-solution, become purple on exposure to light. A silk ribbon, moistened with gold-solution and exposed to light, becomes purple, but does not exhibit any gold colour when polished; if it be then immersed in hydrogen gas, it remains purple in the dark, but on exposure to light, acquires the colour of frosted gold; if, however, it be afterwards kept in the pocket-book, it again becomes purple, possibly because the hydrochloric acid has not been completely washed out. (Creuzburg, *J. pr. Chem.* 10, 380.)—On the addition of potash, nearly all organic compounds reduce gold, precipitating it either immediately, or after some time, in the form of a black powder. The precipitation is accelerated by heat. (H. Rose, *Analyt. Chem.*)

Hydrosulphuric acid passed through either the normal or the acid gold-solution, at ordinary temperatures, throws down tersulphide of gold in dark brown flakes. To the 2000th degree of dilution. (Pfaff.) In a solution containing 1 part of gold in 10,000 parts of liquid, a brownish colour is produced without any precipitate; with from 20,000 to 40,000 parts of liquid, a fainter colour is produced, and with 80,000, a scarcely perceptible colour. (Lassaigne.) When vapour of boiling water, containing a very small quantity of hydrosulphuric acid, is passed through the gold-solution, a purple-brown colouring is first produced, then a purple-red, and lastly a violet. (Pfaff, *Schw.* 52, 318.)—Hyposulphite of soda dropped into excess of gold-solution, throws down sulphide of gold. (Fizeau.)—Iodide of potassium throws down yellow protiodide of gold, with separation of iodine. (Pelletier.) Hydriodic acid darkens the colour of the gold-solution, and after 4 hours, produces a yellow precipitate. (Pleischl, *Schw.* 43, 387.)

Oil of vitriol added to a concentrated normal gold-solution throws down terchloride of gold; on heating the mixture to 150°, the terchloride gives off chlorine gas, and is reduced to protochloride and metallic gold. Similar reactions are produced by aqueous phosphoric and arsenic acid; nitric acid, on account of its ready volatility, has no effect. (Pelletier.) Nitrate or sulphate of silver-oxide, added to the normal gold-solution, precipitates a brownish yellow mixture of auric oxide and chloride of silver, nothing but sulphuric or nitric acid remaining in the liquid. (Pelletier.)—Mercuric nitrate likewise precipitates from the acid gold-solution a yellow powder, which contains auric oxide, calomel, corrosive sublimate, and water, and detonates when heated with sulphur. (Proust.) The precipitate has a dingy green colour, and is not perceptibly altered by boiling the mixture.

Caustic ammonia or carbonate of ammonia added to the gold-solution, throws down the greater part of the gold in the form of fulminating gold; the more acid the gold-solution, and the larger the excess of ammonia added, the greater is the quantity of gold which remains dissolved. Fixed alkalis and magnesia added to the normal or acid gold-solution, in quantity not sufficient for the decomposition of the chloride of gold, darken the colour of the liquid, and after a few hours, produce a reddish

yellow precipitate of hydrated auric oxide, containing chloride of gold and an aurate of the alkali. The precipitation is accelerated by heat; the supernatant liquid contains the alkaline chloride produced in the reaction, together with the chloride of gold which remains undecomposed. Potash, soda, baryta, strontia, or lime, added to the gold-solution in insufficient quantity, precipitates a yellow basic hydrochlorate of auric oxide [impure hydrate, p. 208]; the supernatant reddish yellow liquid still gives a yellow precipitate when heated, but gold likewise remains in solution. (Oberkampf.) Potash added to the gold-solution in quantity not quite sufficient to saturate the acid, colours it reddish yellow at first by withdrawing the excess of acid, and after several hours—more quickly, however, on the application of heat—produces a reddish yellow precipitate. But whether the normal or the acid solution be used, part of the gold always remains dissolved, in the form of chloride of gold and potassium, and gives a reddish yellow colour to the liquid. (Pelletier.) The precipitate dissolves in excess of potash, nothing but a small quantity of brown or blue gold remaining behind. (Vauquelin.) Auric oxide, precipitated by baryta, contains baryta in combination, as well as a little chloride of gold, even if the quantity of baryta added is not sufficient for the complete decomposition of chloride of gold. (Pelletier.) Magnesia added to the gold solution in less than the equivalent quantity, throws down hydrated auric oxide, in combination with a small quantity of magnesia and chloride of gold. The supernatant liquid contains chloride of gold and chloride of magnesium. (Pelletier.) An excess of the fixed alkalis throws down anhydrous auric oxide (more rarely the hydrate) in combination with the precipitating alkali; a certain quantity of gold, however, greater in proportion to the excess of alkali and to the quantity of alkaline chloride in the liquid, remains dissolved in the form of aurate of potash, forming a pale yellow solution. Potash added in excess to the normal solution produces, after a while, a brown-black precipitate of anhydrous auric oxide, the quantity of which increases on heating the liquid. (Oberkampf.) Excess of potash converts the brownish yellow colour first produced in the acid solution, into a greenish yellow, paler in proportion as the excess of potash is greater, and throws down a scanty precipitate of black oxide of gold containing potash; the quantity of this precipitate is less, as that of the potash added is greater, and never exceeds 0·1 of the dissolved gold. The pale greenish yellow liquid contains aurate of potash in combination with chloride of potassium, and when mixed, even with weak acids, assumes the ordinary colour of the gold-solution, inasmuch as chloride of gold and potassium is produced. (Pelletier; *comp.* Frémy, p. 208.) Baryta added in excess to the normal solution at ordinary temperatures, produces a yellow precipitate of basic salt [impure hydrate], but, on the application of heat, it throws down the brown-black, anhydrous oxide; it precipitates the gold more completely than any other alkali; but nevertheless a portion of gold always remains dissolved. (Oberkampf.) Baryta, even in the cold, throws down a black precipitate of anhydrous auric oxide, combined with baryta. The supernatant liquid contains chloride of barium and aurate of baryta. (Pelletier.) Magnesia added in excess to a gold-solution throws down hydrated auric oxide sometimes combined, sometimes merely mixed with baryta; the supernatant colourless liquid contains chloride of barium and aurate of magnesia, and becomes yellow when mixed with hydrochloric acid. Zinc-oxide behaves in the same manner as magnesia. (Pelletier.) If the gold-solution contains much alkaline chloride or free hydrochloric acid, which can form a chloride with the first portions of alkali

added, no precipitate is formed, either by ammonia or by the fixed alkalis. (Oberkampf.) If a normal gold-solution be exactly saturated with carbonate of soda, and boiled, nearly all the gold is precipitated in the form of auric oxide; if the liquid be then supersaturated with carbonate of soda, and neutralized while hot with sulphuric acid, the rest of the auric oxide is precipitated, and the liquid becomes perfectly colourless. (Figuier.) Bicarbonate of potash added to gold-solution at ordinary temperatures does not precipitate the gold, but merely throws down any cupric oxide that may be present. (Duportal & Pelletier, *Ann. Chim.* 78, 47.) Neither monocarbonate nor bicarbonate of potash or soda precipitates gold-solution at ordinary temperatures, in whatever proportion it may be added, but merely produces a deepening of the yellow colour. At the boiling heat, these reagents, if added in small quantity, produce a brownish yellow precipitate, but in excess, they form a clear and nearly colourless liquid. White marble, moistened with gold-solution, does not become coloured in diffused daylight, but if heated or exposed to sunshine, it acquires a purple colour. (Desmarest.)

Phosphate of soda, ferrocyanide and ferricyanide of potassium, and likewise cyanide of mercury, do not precipitate gold-solutions.

## Gold and Nitrogen.

A. *Nitride of Gold?*—By proceeding with sal-ammoniac and chloride of gold, in a manner similar to that described for the preparation of nitride of zinc (V, 33), a black substance is formed at the negative pole, having a specific gravity of 10·3, and so constituted, that a grain of it, when heated, gives off 0·01 cub. in. of nitrogen gas. (Grove.)

B. Nitrate of Auric Oxide, or Auric Nitrate.—*a.* Gold recently precipitated by green vitriol dissolves in strong nitric acid, but often separates from it again when the liquid is agitated. (Bergman & Brandt, *Bergm. Opusc.* 3, 356.)

*b.* According to Tennant (*Scher. J.* 1, 307), fine gold leaves also dissolve in fuming nitric acid, forming an orange-coloured solution. This solution, when shaken up in water, deposits auric oxide; but if it has been previously mixed with excess of fuming nitric acid, or if the water contains a small quantity of nitrate of potash, the gold gives up its oxygen to the nitrous acid, and is precipitated in the metallic state.

*c.* Recently-precipitated auric oxide, or its hydrate, dissolves in strong nitric acid, somewhat more abundantly than in oil of vitriol, and forms a yellowish brown solution. The solution, when evaporated, first deposits auric oxide, and finally leaves a black mixture of auric oxide and metallic gold; water, if no hydrochloric acid is present, precipitates all the auric oxide from it, in the form of a hydrate. (Vauquelin, Pelletier, Frémy.)

C. Aurite of Ammonia.—Formed by treating protoxide of gold with aqueous ammonia.—Violet.—Detonates when heated. (Figuier.)

D. Aurate of Ammonia.—*Fulminating Gold*, *Aurum fulminans.*—1. Auric oxide is converted into fulminating gold by immersion in caustic ammonia, or in sulphate, hydrochlorate, or nitrate of ammonia. In caustic ammonia it gains 23·3 per cent. in weight (Scheele, *Opusc.* 1, 102); in solutions of the above-mentioned ammoniacal salts, it gains 20 per cent.

(Bergman, *Opusc.* 2, 133); and the liquid acquires an acid reaction. (Bergman, Scheele.) Auric oxide prepared by method 3 (p. 207), if immersed for 24 hours in strong ammonia, then washed, and dried at 100°, yields fulminating gold, sometimes of a dark olive-green, sometimes of a lighter green colour, which detonates violently. (Dumas, *Ann. Chim. Phys.* 44, 167.—2. Caustic ammonia or carbonate of ammonia precipitates fulminating gold from a solution of the chloride. The greater the quantity of free acid in the gold-solution, and the larger the excess of ammonia added, the greater is the quantity of gold which remains dissolved.—100 parts of gold treated by this process yield about 125 parts of fulminating gold. (Bergman.) The more completely the fulminating gold is washed —at last by boiling it with water—the more easily and strongly does it detonate; the detonating power is likewise increased by boiling with solution of caustic potash or carbonate of potash, and then washing with water. (Bergman.)—The wash-water forms a cloud with silver-solution, even after three days' washing. (Dumas.) The fulminating gold must be washed with hot water containing ammonia, to remove the chloride of gold. (Berzelius.)—3. From a solution of auric oxide in sulphuric or nitric acid, ammonia likewise throws down fulminating gold. (Bergman.) 4. Potash precipitates fulminating gold from a solution of gold in nitric acid containing sal-ammoniac. (Basilius Valentinus.)

When prepared by the first method, it forms a green powder (Dumas); by the second, third, and fourth, a brownish yellow powder.

| | | | Dumas (1). | | | | Dumas (2). |
|---|---|---|---|---|---|---|---|
| 2N | 28 | 10·89 | 9·0 | 21N | 294·0 | 10·04 | 9.88 |
| 6H | 6 | 2·34 | | 64H | 64·0 | 2·18 | |
| Au | 199 | 77·43 | 76·1 | 11Au | 2189·0 | 74·74 | 73 to 74 |
| 3O | 24 | 9·34 | | 30O | 240·0 | 8·20 | |
| | | | | 4Cl | 141·6 | 4·84 | 4·50 |
| | 257 | 100·00 | | | 2928·6 | 100·00 | |

Fulminating gold prepared by the first method is, according to this analysis, $2NH^3, AuO^3$, or, as Dumas prefers to write it, $NH^3, AuN + 3HO$. —In calculating the formula of fulminating gold prepared by (2), which Dumas washed with cold but not with boiling water, the author has supposed it to be a mere mixture (varying probably according to the temperature during washing) of 1 At. chloride of gold and ammonium with 10 At. of fulminating gold as prepared by (1) : viz. $NH^4Cl, AuCl^3 + 10(2NH^3, AuO^3)$. The calculation must be regarded as merely approximative. The formula assigned by Dumas to the preparation (2) is : $2(NH^3, AuN) + (2NH^3, AuCl) + 9HO$.

Proust found 73 per cent. of gold in fulminating gold prepared by (2). Scheele had previously found that the quantity of oxygen in the gold-oxide of fulminating gold was not sufficient to convert all the hydrogen of the ammonia into water—or, according to the views then entertained—that the phlogiston in the ammonia was more than sufficient to reduce the calx of gold to the metallic state.

Fulminating gold detonates, when rubbed, struck, or heated, or when an electric spark is passed upon it, with a loud, sharp report, and a faint light, and yields nitrogen gas, ammonia, and water.—The facility and violence of the detonation are increased by boiling the powder with water, especially if the water contains caustic potash or carbonate of potash, also by heating it carefully. The explosion may then be brought about even by friction with a strip of paper. [The adhering chlorine-

compound is by these means dissolved or decomposed, and the moisture expelled.]—Fulminating gold kept for some hours at 100°, becomes so inflammable that it can scarcely be touched without exploding. (Dumas.) —Moist fulminating gold does not detonate by heat till it becomes dry, and then not violently and all at once, but in separate portions, as they give off their water. (Bergman.) The detonation by heat takes place at 143°. (Dumas.) Fulminating gold acquires a blackish tint when raised nearly to the temperature at which it explodes. (Bergman.) Even in the explosion of dry fulminating gold, only a portion is decomposed; the rest is merely scattered about, and causes new explosions as it falls on the coal-fire below. (Bergman.)—The explosion breaks through the support, and scatters into the air anything that may be placed upon it. Silver or copper supports are gilded by the explosion. Fulminating gold brought close to a candle from the side puts it out in exploding. The explosion of large masses bursts the doors and windows of the apartment. (Bergman.) A dram of fulminating gold introduced into a bottle, burst it as the stopper was being turned round, small particles of the substance having remained adhering about the mouth; and both the operator's eyes were irrecoverably destroyed by the projected fragments of glass. (Baumé.) Half a dram of fulminating gold exploded in a strong glass vessel yields 0·7 of a cubic inch of nitrogen gas. (Bergman.) A grain of fulminating gold exploded in this manner yields a quantity of nitrogen gas equal in bulk to 1½ drams of water. (Scheele.)—When fulminating gold is carefully mixed with large quantities of finely-divided foreign substances, such as alkaline or earthy salts, the earths, &c., the mixture may be heated without danger of explosion. Oxide of copper behaves in the same manner with fulminating gold; the ignition of the mixture gives rise to the evolution of nitrogen gas; but not of nitric oxide. The residue contains metallic copper and chloride of copper. (Dumas.)—A mixture of 1 pt. of fulminating gold and from 1 to 2 pts. of sulphur does not explode when gradually heated. Fulminating gold may also be introduced by separate small portions into melted sulphur without exploding. (Bergman.) The mixture gradually heated with ten times its weight of sulphur, swells up at 150°, gives off gas, and after the sulphur has burned away, leaves between 73 and 74 parts of metallic gold. When fulminating gold is very carefully heated nearly to the temperature at which it would explode, then cooled a little, and again more strongly heated, great care being taken to avoid friction, it may be ultimately raised to a red-heat without exploding. (Bergman.) Fulminating gold kept for some hours at 130°, then at 140°, and then at 150° and 160°, may afterwards be heated to redness without exploding, all the gold remaining behind in the metallic state. (Dumas.)—Sulphuretted hydrogen gas and aqueous protochloride of tin decompose fulminating gold without detonation, the latter with formation of purple of Cassius. (Proust.)—Fulminating gold remains unaltered when gently heated in oil of vitriol, but if the temperature rises to the boiling point, it is converted, without explosion, into metallic gold; and if the liquid be further concentrated by boiling, sulphate of ammonia sublimes. (Bergman.)—With dilute sulphuric or with nitric acid, it may be boiled without decomposing, the boiling points of these liquids not being so high as that of strong sulphuric acid. (Bergman.)—Boiling hydrochloric acid dissolves fulminating gold sparingly; the portion which remains undissolved is fulminating gold in its original state; and the solution yields a precipitate of that substance when treated with potash. (Bergman.) Copper precipitates gold from the solution, and the remain-

ing liquid distilled with carbonate of potash, yields carbonate of ammonia. (Scheele.)—Aqueous alkalis, most acids, and alcohol, have no effect on fulminating gold, even when heated with it.

If the gold-solution be mixed with an insufficient quantity of ammonia, a yellower fulminating gold is precipitated, which contains chloride of gold as well as aurate of ammonia, detonates at a higher temperature and less violently than pure fulminating gold, and when mixed with 12 parts of silica and heated, yields hydrochloric acid and nitrogen gases. (Berzelius, *Lehrbuch.*)

The supernatant liquid in preparation (2) contains aurate of ammonia, probably combined with the hydrochlorate of ammonia in the form of a double salt.

The solution of teriodide of gold in aqueous hydriodic acid, forms, with ammonia, a precipitate which is dark brown or black, accordingly as the ammonia or the gold-solution is in excess, and, when heated, detonates like fulminating gold, giving off iodine and ammonia. Hot nitric acid converts it, with evolution of iodine, into a mixture of metallic gold and the protiodide. (Johnston.)

E. Iodo-aurate of Ammonium.—The solution obtained by digesting teriodide of gold in hydriodate of ammonia, yields black, strongly lustrous, flat, four-sided prisms, which deliquesce in moist air. (Johnston.)

F. Chloro-aurate of Ammonium.—*a. Yellow.*—The neutral solution of chloride of gold, mixed with sal-ammoniac, yields, by spontaneous evaporation, golden-yellow, transparent needles, or right rectangular prisms with quadrilateral summits, or large rhombic tables.—The crystallized salt, when exposed to the air, begins to effloresce, even in a few minutes.—When heated a little above 100°, it gives off all its water and becomes darker, but resumes its pale yellow colour on cooling. At a higher temperature, it fuses into a reddish liquid, giving off chlorine and sal-ammoniac, and leaving gold. If the heat be carefully applied, this decomposition takes place without fusion, so that the gold still retains the form of the crystals. (Johnston.)

*b. Red.*—1. The yellow salt dissolves with effervescence in hot aqua-regia, forming sometimes a reddish yellow, sometimes a deep blood-red liquid, which, on cooling, deposits yellow prisms, similar to those of *a*, but acquiring a deep red colour at 149°. On evaporating the solution, there remains a blood-red mass—or deep purple-red, if the temperature be raised to the point of incipient decomposition—which, when exposed to the air, deliquesces very rapidly and forms a yellow liquid; and this, when evaporated, leaves a red liquid, which solidifies on cooling in a mass consisting of dark red needles. Alcohol poured upon this mass separates sal-ammoniac and greenish yellow gold-particles, and forms a dark red solution, which, on evaporation, yields reddish yellow, four-sided prisms. These crystals turn red at 100°, fuse at a somewhat higher temperature, and then solidify in a mass, which, when examined by the microscope, is found to be made up of cubes. Alcohol dissolves these cubes in the same manner as the original mass, but only partially. The aqueous solution is not decomposed by alcohol. Ammonia forms with it a light brown precipitate.—2. By evaporating a mixture of sal-ammoniac and acid gold-solution [likewise containing nitric acid?] in a glass, with frequent stirring and at a high temperature, so that the yellow salt which collects on the sides may dissolve with effervescence in the

liquid. The liquid, on further evaporation, becomes blood-red, and when cooled, yields a great number of bright red cubes, with which, at a later stage of the operation, small yellow prisms of the yellow salt *a* become mixed. The cubes, when kept in a sealed tube, turn yellow in a few weeks without change of form. (Johnston.)

The sublimate which Storr obtained (*Crell. N. Entd.* 2, 40) by heating ½ oz. (1 loth) of sal-ammoniac with 21 gold-leaves, exhibited a purple colour in particular places, formed a solution of the same colour with water, and the solution, when left to stand for some time, or mixed with carbonate of potash, yielded a purple precipitate.

## Gold and Potassium.

A. Alloy of Gold and Potassium.—Potassium acts rapidly on gold at high temperatures. Water extracts potash from the compound, leaving the gold unaltered. (H. Davy.)

B. Aurite of Potash.—When protochloride of gold is decomposed by solution of potash, part of the resulting protoxide dissolves in the potash, forming a green solution; the compound is, however, soon resolved into metallic gold which gilds the sides of the vessel, and aurate of potash. (Berzelius.)

C. Aurate of Potash.—When nitre is melted for a long time in a golden tube, the potash thereby produced forms a yellow solution in water. This solution, when mixed with nitric or sulphuric acid, acquires a darker colour, and deposits metallic gold, the reduction being probably due to the nitrite of potash present in the liquid. (Tennant, *Scher. J.* 1, 306.)

Pelletier, by boiling the hydrated auric oxide precipitated by magnesia and exhausted by boiling water (it still contained magnesia), or the hydrate precipitated by water from the nitric acid solution, with caustic potash, obtained an alkaline liquid, which crystallized indistinctly on evaporation, depositing at the same time a small quantity of anhydrous auric oxide, and when supersaturated with hydrochloric acid, yielded a yellow gold-solution; when mixed with excess of sulphuric or nitric acid, it gave a yellow flocculent precipitate of hydrated auric oxide, which soon turned violet, and when the liquid was further concentrated, became black. If, however, the aurate of potash had been previously mixed with a metallic chloride, sulphuric or nitric acid formed a clear yellow mixture.—According to the more recent observations of Figuier, it remains to be determined whether the liquids obtained by Tennant and Pelletier may not contain peraurate of potash.—Aurate of potash (or soda) obtained, either by boiling a solution of chloride of gold with excess of monocarbonate or bicarbonate of potash (or soda), or by boiling auric oxide precipitated by magnesia with solution of potash (or soda), gilds copper, brass, and bronze, and is peculiarly well adapted for that purpose (*vid.* Elkington, *Pogg.* 55, 160; Schubarth, *J. pr. Chem.* 11, 339).

¶. Frémy obtains aurate of potash in the crystalline state by evaporating the solution of pure auric oxide (auric) acid in a slight excess of pure potash, first over the open fire and then in vacuo. If the liquid is very concentrated, the aurate of potash crystallizes in small needles, having a faint yellowish colour and arranged in warty groups; the liquid

often solidifies in a mass on slight agitation. To free the crystals from a certain quantity of potash or carbonate of potash which often adheres to them, they must be quickly washed with cold distilled water, or else recrystallized, which is better; the crystals are laid on unglazed porcelain, and dried in vacuo. During the evaporation, a certain quantity of gold generally separates, and must be removed by decantation. Aurate of potash is very soluble in water, imparting to it a slight yellowish colour, and a strong alkaline reaction.

| | | | | | Frémy. |
|---|---|---|---|---|---|
| KO | 47·2 | .... | 14·54 | .... | 14·1 |
| Au | 199·0 | .... | 61·43 | .... | 61·1 |
| 3O | 24·0 | .... | 7·39 | .... | 7·5 |
| 6HO | 54·2 | .... | 16·64 | .... | 16.7 |
| $KO,AuO^3+6Aq$ .... | 324·2 | .... | 100·00 | .... | 99·4 |

Decomposes at a gentle heat, with a kind of decrepitation, giving off oxygen and water, and leaving a residue of metallic gold and potash, generally mixed with peroxide of potassium. Nearly all organic substances reduce aurate of potash, precipitating metallic gold; attempts to moderate the action of the reducing agents, in such a manner as to obtain potash-salts containing a lower oxide of gold, were unsuccessful.—Aurate of potash gives precipitates with most metallic salts, showing that the corresponding aurates are insoluble in water. Many of them, however, are soluble in excess of the reagent; thus, chloride of calcium forms with aurate of potash a precipitate of aurate of lime soluble in excess of chloride of calcium. (Frémy, *N. Ann. Chim. Phys.* 31, 478.) ¶

Aurate of potash appears to be capable of combining with other potash-salts to form double salts.

As auric oxide precipitated by potash from the gold-solution retains a portion of potash so obstinately that it cannot be extracted by water but only by nitric acid, there must likewise exist an insoluble *aurate of potash with excess of auric acid.*

D. Sulphide of Gold and Potassium.—*Aurosulphuret of Potassium.*—Gold dissolves in fused potassic liver of sulphur.—¶ When 1 At. gold, 2 At. protosulphide of potassium, and 6 At. sulphur are melted together in a crucible, a fused mass is obtained, which, when digested in water, yields a solution probably containing the compound KS, AuS; this solution, when evaporated, yields a mass of indistinct crystals, the composition of which could not be correctly determined by analysis. (Yorke.) ¶—Aqueous sulphide of gold and potassium is obtained: 1. By dissolving sulphide of gold in a hot aqueous solution of sulphide of potassium, or of caustic potash.—2. By boiling finely-divided gold and sulphur with hydrosulphate of potash, caustic potash, or carbonate of potash. Hydrosulphate of potash does not dissolve gold without the addition of sulphur.—3 parts of sulphur and 3 parts of crude potash dissolve 1 pt. of gold when boiled with it in water. (Stahl.)—Acids added to the reddish yellow solution of sulphide of gold and potassium, precipitate sulphide of gold in the form of a brown powder. (Oberkampf.)

¶ E. Aurosulphite of Potash.—When sulphite of potash is added drop by drop to a solution of aurate of potash previously mixed with excess of alkali, the liquid first acquires a brown colour, and immediately afterwards this salt crystallizes out in beautiful yellow needles. These crystals are nearly insoluble in the alkaline liquid; but pure water, especially at a

boiling heat, decomposes and dissolves them, with evolution of sulphurous acid and separation of metallic gold. Acids decompose this salt immediately, likewise causing an escape of sulphurous acid and precipitation of gold. Organic substances also reduce the gold. After drying in vacuo, the salt may be preserved in well-stopped bottles for two or three months, but not longer; even in sealed tubes, it ultimately decomposes, sulphurous acid being liberated, and a blackish mass left, chiefly consisting of metallic gold and sulphate of potash. The same decomposition is rapidly brought about by heat. (Frémy.)

| | | | | | Frémy. |
|---|---|---|---|---|---|
| $5KO$ | 236 | .... | 31·06 | .... | 29·5 |
| $AuO^3$ | 223 | .... | 29·34 | .... | 29·1 |
| $8SO^2$ | 256 | .... | 33·68 | .... | 37·0 |
| $5HO$ | 45 | .... | 5·92 | .... | |
| $KO,AuO^3+4(KO,2SO^2)+5Aq$ | 760 | .... | 100·00 | | |

This salt might also be regarded as sulphite of auric oxide and potash: $5(KO,SO^2)+AuO^3,3SO^2+5$ Aq.; considering, however, the little tendency which auric oxide has to combine with acids, it is not very likely that it should unite with so powerful a reducing agent as sulphurous acid. Frémy is most inclined to regard this compound as the potash-salt of a ternary acid composed of gold, sulphur, and oxygen, analogous to his sulphazotic acid. (*Ann. Pharm.* 56, 315.) ¶.

F. Iodo-aurate of Potassium.—1. Formed by adding nearly 1 At. terchloride of gold (with agitation) to 4 At. iodide of potassium dissolved in water, and leaving the dark-coloured liquid to crystallize:

$$4KI+AuCl^3=3KCl+(KI,AuI^3).$$

2. Teriodide of gold dissolves abundantly in hot aqueous iodide of potassium, forming a dark red-brown liquid which yields the same crystals. (Johnston.) The solution of protiodide of gold in aqueous iodide of potassium (the formation of which is attended with separation of gold), when evaporated over the water-bath, and even at lower temperatures, gives off iodine and deposits gold, but nevertheless sometimes yields crystals of the double iodide. (Fordos.)—Long, slender, four-sided prisms, striated on the two lateral faces, and with dihedral summits. Strongly lustrous, black and opaque, even by candle-light. At 66° they give off part of their iodine, and acquire a purple colour. When exposed to the air at ordinary temperatures, they give it off very slowly. When heated in a tube, they yield a skeleton of gold, which still retains the crystalline form. In water they dissolve with partial decomposition; aqueous hydriodic acid and very dilute iodide of potassium dissolve them perfectly. (Johnston.)

| | *Crystallized.* | | | | Johnston. |
|---|---|---|---|---|---|
| KI | 165·2 | .... | 22·26 | .... | 22·27 |
| Au | 199·0 | .... | 26·81 | .... | 26·71 |
| 3I | 378·0 | .... | 50·93 | .... | 51·02 |
| $KI,AuI^3$ | 742·2 | .... | 100.00 | .... | 100·00 |

G. Bromo-aurate of Potassium.—Formed by mixing aqueous terbromide of gold with bromide of potassium. The solution of the dehydrated salt in absolute alcohol, deposits, when evaporated by heat, anhydrous crystals, having the form of rhombic prisms and irregular six-sided prisms, and the same colour as the hydrated salt.—The aqueous solution yields hydrated crystals, which are also right rhombic

prisms. *Fig.* 61; $u' : u = 102° 30'$. By reflected light they exhibit a semi-metallic lustre and the colour of specular iron; by transmitted light they appear of a fine purple-red. In dry air they effloresce, assuming the appearance of blood-stone; they give off all their water at 60°. They dissolve sparingly in water, forming a deep reddish yellow-brown solution,—more readily in alcohol. (Bonsdorff, *Pogg.* 19, 346; 33, 64.)

| | *Anhydrous.* | | | | *Hydrated.* | | | |
|---|---|---|---|---|---|---|---|---|
| KBr | 117·6 | .... | 21·31 | | KBr | 117·6 | .... | 19·71 | .... | 20·16 |
| Au | 199·0 | .... | 36·06 | | Au | 199·0 | .... | 33·34 | .... | 33·12 |
| 3Br | 235·2 | .... | 42·63 | | 3Br | 235·2 | .... | 39·41 | .... | 39·84 |
| | | | | | 5HO | 45·0 | .... | 7·54 | .... | 6·88 |
| $KBr, AuBr^3$ | 551·8 | .... | 100·00 | | +5Aq. | 596·8 | .... | 100·00 | .... | 100·00 |

H. Chloro-aurite of Potassium.—KCl, AuCl.—Formed by fusing the chloro-aurate.—In the fused state, this compound is black-brown, translucent at the edges, where it exhibits a dark brown colour; when cold it is yellow. In a close vessel it sustains a continued red heat without decomposing. When digested in water (or hydrochloric acid) it is resolved into metallic gold and a soluble mixture of chloride and chloro-aurate of potassium. (Berzelius.)

I. Chloro-aurate of Potassium.—By evaporating and cooling a solution of chloride of gold mixed with chloride of potassium, yellow, hydrated crystals are obtained (Javal), which give off their water at 100°, and are reduced to a lemon-yellow powder (Berzelius).—At a higher temperature the salt fuses into a dark red-brown liquid, and is converted, with loss of chlorine, into the compound H. (Berzelius); and when kept for a long time at the temperature of melting glass, it is resolved into a mixture of gold and chloride of potassium, a portion, however [in the form of the salt H], remaining undecomposed. (Javal.) Hydrogen gas passed over the salt at a red-heat, decomposes it completely, yielding hydrochloric acid gas and a mixture of gold and chloride of potassium. (Berzelius & Johnston.)

The hydrated crystals are yellow four-sided prisms (Javal), orange-yellow rhombic prisms with striated surfaces, or needles, or large six-sided tables. (Berzelius & Johnston.) According to Berzelius, the prisms are perpendicularly truncated; according to Johnston, obliquely. A very acid solution yields thick prisms; a neutral solution, needles; and a solution supersaturated with chloride of potassium, and left to evaporate spontaneously, yields tables (Berzelius & Johnston).—The crystals effloresce slightly when exposed to the air (Javal, Johnston); they effloresce very quickly in dry air, yielding a sulphur-yellow powder; at 100° they give off all their water without a trace of chlorine. (Berzelius, *N. Edinb. J. of Sc.* 3, 281; also *Pogg.* 18, 599.) At 100° they give off only 8 per cent., and do not evolve any more till heated to the point at which chlorine likewise begins to go off; they then give off at most 9·43 p. c. (Johnston, *N. Edinb. J. of Sc.* 3, 290.) The crystals dissolve readily in water, forming a bright yellow solution. (Javal, *Ann. Chim. Phys.* 17, 337; also *N. Tr.* 6, 2, 285.) They are also easily soluble in alcohol. (Berzelius.)

| | *Anhydrous.* | | |
|---|---|---|---|
| KCl | 74·6 | .... | 19·64 |
| Au | 199·0 | .... | 52·40 |
| 3Cl | 106·2 | .... | 27·96 |
| $KCl, AuCl^3$ | 379·8 | .... | 100·00 |

| | Crystallized. | | Berzelius. | | Johnston. | | Javal. |
|---|---|---|---|---|---|---|---|
| KCl | 74·6 | 17·57 | 17·53 | 18·38 | | 24·26 |
| Au | 199·0 | 46·84 | 46·80 | 46·73 | | 68·64 |
| 3Cl | 106·2 | 25·00 | 25·05 | 25·44 | | |
| 5HO | 45·0 | 10·59 | 10·62 | 9·45 | | 7·10 |
| $KCl,AuCl^5 + 5Aq$ | 424·8 | 100·00 | 100·00 | 100·00 | | 100·00 |

A red solution is obtained by dissolving the salt I in aqua-regia; but this solution yields on evaporation, not a red mass, but yellow crystals which do not turn red even when heated. (Johnston.)

K. Aurate of Potash with Chloride of Potassium?—When a gold-solution is precipitated by excess of potash (or carbonate of potash), there remains a pale green liquid, which, on evaporation, yields crystals of chloride of potassium mixed with yellow crystals (Vauquelin); all acids, even very weak ones, colour it yellow by withdrawing potash and separating chloride of gold. The addition of an excess of potash produces no further precipitate in the liquid. (Oberkampf, Pelletier.)—A mixture of the solution of chloride of gold and an alkaline carbonate is reduced by sugar on the application of a gentle heat. (Döbereiner, *Ann. Pharm.* 2, 5.)—Pelletier supposes that the gold-solution, after precipitation by excess of potash, contains independently: chloride of potassium, chloride of gold, and aurate of potash.—According to Figuier's experiments it probably contains peraurate of potash, together with chloride of potassium and aurate of potash.

According to Pelletier, auric oxide dissolves in small quantity in a boiling aqueous solution of chloride of potassium; the liquid is yellowish and has a slight alkaline reaction; it therefore probably contains terchloride of gold, aurate of potash, and chloride of potassium (chemically combined?)

## Gold and Sodium.

¶ A. Sulphide of Gold and Sodium.—*Aurosulphuret of Sodium.*—1. Formed by heating to bright redness a mixture of 1 At. gold, 2 At. protosulphide of sodium, and 6 At. sulphur, digesting the fused mass in water, filtering the resulting yellow solution in an atmosphere of nitrogen, and concentrating in vacuo over sulphuric acid; yellow crystals are thereby obtained, which become colourless by recrystallization.—2. By dissolving sulphide of gold (obtained by treating a solution of the chloride with sulphuretted hydrogen, and probably consisting of $AuS^2$) in aqueous protosulphide of sodium, and leaving the solution to crystallize. —The crystals belong to the oblique prismatic (monoclinometric) system; they are six-sided prisms, with trilateral or quadilateral summits. They quickly turn brown in the air, and when heated, give off water, and afterwards sulphur. They are soluble in water and alcohol. Acids added to the solution throw down a yellowish brown precipitate, containing 1 At. gold and from 1 to 2 At. sulphur, sulphuretted hydrogen being likewise evolved. The solution, when exposed to the air, slowly decomposes and turns brown. (Yorke, *Chem. Soc. Qu. J.* 1, 236.)

| | | | Yorke (*mean*). |
|---|---|---|---|
| Au | 199·0 | 60·75 | 60·04 |
| Na | 23·2 | 7·10 | 7·31 |
| 2S | 32·0 | 9·89 | 10·36 |
| 8HO | 72·0 | 22·26 | 21.94 |
| NaS,AuS + 8Aq | 326·2 | 100·00 | 99·65 |

Sulphide of hydrogen and sodium, digested with sulphide of gold, dissolves but a very small quantity of it at ordinary temperatures; on heating the solution, the sulphide of gold is reduced. (Yorke.)

B. Hyposulphite of Aurous Oxide and Soda.—*a.* When terchloride of gold and hyposulphite of soda are dissolved in very small quantities of water, the solutions mixed, and alcohol added, a precipitate is formed, consisting of this salt, while tetrathionate of soda and chloride of sodium remain in solution:

$$8(NaO,S^2O^2) + AuCl^3 + 4HO = [3(NaO,S^2O^2) + AuO,S^2O^2 + 4Aq] + 2(NaO,S^4O^5) + 3NaCl.$$

By redissolving the precipitate in a small quantity of water, and reprecipitating with alcohol, the salt is obtained in a state of purity; it then forms colourless needles, insoluble in strong alcohol, very easily soluble in water, and having a sweet taste.

| | | | Fordos & Gélis. |
|---|---|---|---|
| Au | 199·0 | 37·65 | 37·35 |
| 3Na | 69·6 | 13·17 | 13·27 |
| 8S | 128·0 | 24·21 | 24·33 |
| 12O | 96·0 | 18·16 | 18·35 |
| 4HO | 36·0 | 6.81 | 6·70 |
| $3(NaO,S^2O^2) + AuO,S^2O^2 + 4Aq$ | 528·6 | 100·00 | 100·00 |

The salt, when heated in a tube, first gives off water, then sulphur and sulphurous acid; the water does not go off at 100°; but between 150° and 160°, the salt loses from 6·4 to 7·0 per cent. of water without decomposition. When exposed to the air, it takes up this water again in the course of 24 hours. Decomposes when suddenly heated, leaving metallic gold and sulphate of soda: it is free from chlorine. Nitric acid acts rapidly upon it, forming sulphuric acid; sulphuretted hydrogen and soluble metallic sulphides precipitate the solution brownish yellow.—Tincture of iodine forms no precipitate in a concentrated solution of this salt; but on diluting with a large quantity of water, after saturation, pure yellow protiodide of gold is immediately precipitated, while iodide of sodium and tetrathionate of soda remain in the liquid:

$$[3(NaO,S^2O^2) + AuO,S^2O^2] + 2I = AuI + NaI + 2(NaO,S^4O^5).$$

The protiodide of gold is subsequently resolved by the action of the dissolved iodide of sodium into metallic gold and the teriodide; but its precipitation in the first instance, free from teriodide, shows that the original salt contains no teroxide of gold.—The presence of gold in this salt is not indicated by green vitriol, protochloride of tin, or oxalic acid. Hydrochloric acid, dilute sulphuric acid, and vegetable acids added to the solution, neither separate sulphur nor sulphurous acid; nitric acid alone decomposes it at ordinary temperatures. Chloride of barium throws down a precipitate somewhat soluble in water, but completely separable on the addition of alcohol; this precipitate probably consists of a hyposulphite of aurous oxide and baryta corresponding to the soda-salt.

A solution of this salt, containing from 1 to 1½ pt. in 1000 parts of water, is recommended by Fordos and Gélis for fixing the pictures on Daguerreotype plates, instead of the usual mixture of chloride of gold (1 pt. in 500 of water) and hyposulphite of soda (3 pts. in 500).

By the further action of hyposulphite of soda on chloride of gold, other products are formed; and among the rest, a brown substance soluble

in water and insoluble in alcohol; it appears to be richer in gold than the salt above described, and when the chloride of gold is in excess, is resolved into sulphuric acid and metallic gold. (Fordos & Gélis, *N. Ann. Chim. Phys.* 13, 394.)

*b.* Another hyposulphite of aurous oxide and soda, containing $3NaO,S^2O^2+AuO,S^2O^2+5$ Aq. is mentioned by Himly. (*Ann. Pharm.* 59, 95.) ¶

C. Hyposulphite of Auric Oxide and Soda.—Formed by dropping a solution of chloride of gold free from excess of acid into aqueous hyposulphite of soda, the latter being somewhat in excess. If an excess of gold-solution be added, sulphide of gold is precipitated. The mixture assumes a reddish tint at first, but soon becomes colourless. It contains no sulphuric acid, but appears to contain tetrathionate of auric oxide and soda, as well as hyposulphite. (Fordos & Gélis, *N. J. Pharm.* 4, 338.)

¶ D. Sulphite of Aurous Oxide and Soda?—Colourless in solution, but when precipitated by alcohol, it is yellow, like fulminating gold by reflected light, and red like gold-purple by transmitted light. With nitrate of silver it gives a precipitate having the colour of chromate of lead, and with lead-salts, a red, perfectly insoluble compound. In composition it corresponds to the hyposulphite B, *b*. (Himly.) ¶

E. Iodo-aurate of Sodium.—The solution of teriodide of gold in aqueous iodide of sodium, obtained by digestion, yields highly deliquescent, strongly lustrous, black, four-sided prisms. (Johnston.)

F. Bromo-aurate of Sodium.—Has the aspect and colour of the corresponding potassium-salt; appears not to effloresce; dissolves slowly in water, forming a reddish yellow-brown solution. (Bonsdorff.)

G. Chloro-aurate of Sodium.—Formed by evaporating to dryness the solution of 4 parts of gold in aqua-regia, dissolving the residue in 8 parts of water, adding 1 part of common salt, evaporating the liquid down to 4 parts, and leaving it to crystallize by cooling. If a large quantity of common salt be added, the excess crystallizes out separately; if the quantity be smaller, free chloride of gold remains in the mother-liquid. (Figuier, *J. Pharm.* 6, 84; 8, 157; also *Repert.* 14, 169; *Schw.* 35, 342; *N. Tr.* 6, 2, 301; and 8, 218.)—Long, orange-yellow, four-sided prisms (Figuier); large rhombic prisms and tables (Berzelius & Johnston). Aurora-red, four-sided prisms, acuminated with four faces and again truncated; or six-sided prisms. (Bley, *N. Br. Arch.* 22, 70.)—The crystals are permanent in the air. (Figuier.) They give off their water with difficulty; after two hours' careful heating, they lose only 1·12 per cent. of water; and to drive off all the water, strong and continued heating is required, in which case chlorine is likewise given off. (Berzelius & Johnston.) At a red-heat, the salt gradually evolves chlorine, but a long-continued heat is required to decompose the chloride of gold completely. (Figuier.)

| | *Anhydrous.* | | |
|---|---|---|---|
| NaCl | 58.6 | .... | 16·11 |
| Au | 199·0 | .... | 54·70 |
| 3Cl | 106·2 | .... | 29·19 |
| $NaCl,AuCl^3$ | 363·8 | .... | 100·00 |

| | *Crystallized.* | | | | Berzelius & Johnston. | | Thomson. | | Figuier. |
|---|---|---|---|---|---|---|---|---|---|
| NaCl | 58·6 | .... | 14·66 | .... | 14·47 | .... | 14·85 | .... | 14·1 |
| Au | 199·0 | .... | 49.78 | .... | 49·50 | .... | 49·51 | .... | 69·3 |
| 3Cl | 106·2 | .... | 26·56 | .... | 26·50 | .... | 17·82 | | |
| 4HO | 36·0 | .... | 9·00 | .... | 9·53 | .... | 17·82 | .... | 16·6 |
| $NaCl,AuCl^3+4Aq.$ | 399·8 | .... | 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·0 |

By treating the salt with aqua-regia, according to the first process described on page 225, with reference to chloro-aurate of ammonium, a red salt is obtained of precisely corresponding character, excepting that the saline mass which remains on evaporation is not purple, but blood-red. (Johnston.)

H. Aurate of Soda with Chloride of Sodium.—Similar to the corresponding potassium-compound. Auric oxide likewise dissolves in a boiling solution of common salt in the same manner as in solution of chloride of potassium. (Pelletier.)

## Gold and Lithium.

Chloro-aurate of Lithium.—A solution of chloride of gold evaporated with chloride of lithium, yields orange-yellow, four-sided needles. If the chloride of lithium contains chloride of potassium, chloro-aurate of potassium separates out first. The crystals of the lithium-salt are highly deliquescent, become opaque at 100° from loss of water; and when heated over a spirit-lamp, are completely decomposed into chlorine gas and a mixture of gold and chloride of lithium. (Johnston.)

## Gold and Barium.

A. Aurate of Baryta.—When a normal solution of chloride of gold is mixed with baryta-water, a compound is precipitated, containing a large proportion of auric oxide united with baryta, and a small quantity of hydrochloric acid, which latter substances cannot be extracted by water, but only by strong nitric acid, which must be afterwards diluted to separate the auric oxide. (Pelletier.)

¶ B. Hyposulphite of Aurous Oxide and Baryta ?—Analogous to the soda-salt B, *a*. (p. 251.) Slightly soluble in water, but insoluble in alcohol. When treated with sulphuric acid, it yields an acid salt containing AuO, uncrystallizable, strongly acid, and slightly decomposible at ordinary temperatures. (Fordos & Gélis.) ¶

C. Iodo-aurate of Barium.—Teriodide of gold dissolves in iodide of barium, forming a red-brown solution.

D. Bromo-aurate of Barium.—Red-brown prisms, permanent in the air. (Bonsdorff.)

E. Chloro-aurate of Barium.—Yellow, rhombic prisms, shortened into tables. *Fig.* 61, $u' : u = 105°$. Permanent in dry air, deliquescent in moist air. (Bonsdorff.)

E. Aurate of Baryta with Chloride of Barium?—When a solution of chloride of gold is precipitated by excess of baryta, there remains a colourless liquid, which, when evaporated in the air, deposits a violet mixture of auric oxide and carbonate of baryta. (Pelletier.)—Gold-solution previously mixed with a sufficient quantity of chloride of barium, gives no precipitate with baryta-water. (Oberkampf.) Auric oxide dissolves in a boiling solution of chloride of barium, in the same manner as in chloride of potassium. (Pelletier.)

When sulphate of baryta is precipitated by sulphuric acid from a gold-solution mixed with chloride of barium, all the auric oxide goes down with it. (Berzelius, *Ann. Chim. Phys.* 14, 376.)

## Gold and Strontium.

A. Iodo-aurate of Strontium.—Aqueous iodide of strontium dissolves teriodide of gold, forming a red-brown liquid. (Johnston.)

B. Chloro-aurate of Strontium.—Yellow rhombic prisms permanent in the air. (Bonsdorff.)

C. Aurate of Strontia with Chloride of Strontium.—A solution of chloride of gold mixed with a sufficient quantity of chloride of strontium is no longer precipitable by strontia-water. (Oberkampf.)

## Gold and Calcium.

A. Chloro-aurate of Calcium.—Long rhombic prisms united in radiating masses, permanent in dry air, deliquescent in ordinary air. (Bonsdorff.)

| | *Anhydrous.* | | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|---|
| CaCl ..... | 55·4 | .... | 15·36 | CaCl .... | 55·4 | .... | 13·36 | ..... 13·70 |
| $AuCl^3$ ..... | 305·2 | .... | 84·64 | $AuCl^3$ .... | 305·2 | .... | 73·61 | ..... 71·53 |
| | | | | 6HO .... | 54·0 | .... | 13·03 | ..... 14·77 |
| $CaCl,AuCl^3$ | 360·6 | .... | 100·00 | + 6Aq.... | 414·6 | .... | 100·00 | .... 100·00 |

B. Aurate of Lime with Chloride of Calcium.—Analogous to the strontium-compound.

## Gold and Magnesium.

A. Aurate of Magnesia.—Magnesia heated with the normal solution of chloride of gold, throws down aurate of magnesia. If the magnesia is not in excess, the precipitate contains hydrated auric oxide, magnesia, and chloride of gold. If the magnesia is in excess, a portion of the superabundant quantity likewise mixes with the precipitate. Nitric acid dissolves out the magnesia, leaving a residue of hydrated or anhydrous auric oxide, accordingly as the acid is dilute or concentrated. (Pelletier.)

B. Bromo-aurate of Magnesium.—Dark brown rhombic prisms, slightly translucent, and exhibiting a reddish tint by transmitted light: they are permanent in dry, but deliquesce in moist air. (Bonsdorff.)

C. Chloro-aurate of Magnesium.—Short rhombic prisms of a lemon-yellow colour. (*Fig.* 61) $u' : u = 108°$. When gently heated, they give off their water of crystallization, and fuse into a dark brown liquid which gives off chlorine, and finally dries up. Permanent in a dry winter air, but deliquescent in summer air. (Bonsdorff.)

| *Anhydrous.* | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|
| MgCl | 47·4 | 13·44 | MgCl | 47·4 | 10·29 | 11·0 |
| $AuCl^3$ | 305·2 | 86·56 | $AuCl^3$ | 305·2 | 66·26 | 64·5 |
| | | | 12HO | 168·0 | 23·45 | 24·5 |
| $MgCl,AuCl^3$ | 352·6 | 100·00 | +12Aq. . | 460·6 | 100·00 | 100·0 |

D. Aurate of Magnesia with Chloride of Magnesium ?—When a hot solution of chloride of gold has been precipitated by excess of magnesia, there remains a colourless liquid, which contains a small quantity of auric oxide, and turns yellow when mixed with hydrochloric acid. (Pelletier.)

## Gold and Silicium.

Glass-flux coloured by Gold.—*Ruby-glass.*—Finely-divided metallic gold, chloride of gold, fulminating gold, the precipitate thrown down from a solution of the chloride by potash or soluble glass, the purple of Cassius, &c., fused at a continued gentle heat, with a glass containing oxide of lead, impart to it, according to circumstances, a yellow or a purple-red colour.

As the theory of ruby-glass is at present involved in great obscurity, some supposing it to contain the yet undetermined red oxide of gold, while others, with less probability, suppose it to contain very finely divided metallic gold, it will be sufficient to collect together the more important observations relating to its preparation and properties :

A glass-flux is prepared from 5 parts of quartz-powder, 8 of red-lead, 1 of carbonate of potash, and 1 of nitre; it is then poured out of the pots into water and beaten. One pound of this flux is mixed with 3 loth (6 oz.) of crystallized borax, 45 grains of stannic oxide (this is essentially necessary), 45 grains of antimonic oxide (which is superfluous), and a solution of $\frac{1}{80}$ of a ducat in aqua-regia. This mixture is fused for 12 hours (or for a shorter time) at a very gentle heat, the glass-pot left to cool in the annealing furnace, and broken to pieces when cold: the product thus obtained is crude ruby-glass having the colour of topaz. This substance, when gently heated—contact of smoke not being at all necessary, but rather prejudicial—gradually assumes a red colour throughout its mass; this reddening takes place even during the shaping of the glass in the working aperture. When ruby-glass which has been reddened by heat is fused, it completely loses its purple colour, and becomes marked with liver-coloured spots, which are nothing more than reduced gold in a fine state of division. If the glass is deficient in stannic oxide, which should amount to at least 30 grains for $\frac{1}{80}$ of a ducat, the red colour produced is fainter, and liver-coloured spots are formed. (Fuss, *J. pr. Chem.* 7, 417.)

Purple of Cassius mixed and fused with borax, white glass, or lead-glass, remains within it unaltered, till the temperature reaches the melting point of gold, at which point globules of gold separate from it, and collect at the bottom of the crucible. At a stronger heat, the glass acquires a yellow colour; when still more strongly heated, it gradually becomes

brownish-yellow, green, and bluish-green; and when exposed for eight hours to a yet higher temperature in a strongly drawing air-furnace, it becomes orange-coloured, aurora-red, and purple. After slow cooling, the mass is colourless or yellow, but becomes purple or violet when heated till it softens.—In the glass-works, the purple of Cassius is fused with a flux into the form of a turbid, yellow glass, which is then added to the mass of glass to be coloured, and the fused product poured out into water, whereby a topaz-yellow glass is obtained, penetrated with brilliant granules of gold. This fusion and pouring out into water is repeated from four to six times, till the glass acquires a purple-red colour, and no longer exhibits globules of gold. The gold which separates at the beginning of the fusion is therefore gradually taken up by the glass, and imparts to it a yellow colour when in small, and a red colour when in larger quantity.—The stannic oxide is quite superfluous; metallic gold, chloride of gold, or fulminating gold, yields the same colours with glass [free from tin ?] and indifferently with or without the contact of air and oxidizing agents. Everything depends on the strength and duration of the heat. The violet purple of Cassius, which contains more stannic oxide than the red, does not directly form a violet glass. Part of the stannic oxide is reduced to the state of metal, which sinks to the bottom, and another portion forms an enamel which partly rises in the form of scum, and is partly deposited on the sides of the crucible. The stronger the heat, the smaller is the quantity of reduced tin, and the greater the quantity of enamel obtained. Glass saturated with gold is opaque and yellow, and by itself is incapable of assuming any other colour. It requires to be fused at a continued strong heat with a larger quantity of crystal-glass; the mixture thus obtained is yellow, paler in colour the larger the quantity of crystal-glass added; it is sometimes even colourless. At the softening temperature, the yellow glass assumes a carmine-red, the colourless glass a wine-red colour. Glass which has been reddened by the softening heat becomes colourless when heated to the melting point. When again heated to the softening point, it becomes violet; and if these alternations be continued, the glass being first softened at a gentle heat and then fused, it finally becomes blue at the softening temperature. At length, however, it becomes colourless when fused, and no longer acquires a blue colour at the softening heat, unless it be ignited very strongly and for a very long time, in order to diffuse the gold uniformly through it. (Golfier; Besseyre, *Ann. Chim. Phys.* 54, 48.)

Any gold-precipitate fused in the glass-furnace with soft crystal-glass, yields a transparent and colourless glass, pieces of which, when heated to redness in a retort, and therefore out of contact of all reducing agents, acquire a purple-red colour. (Proust, *N. Gehl.* 1, 504.)

¶ Among the various explanations which have been suggested for the red colouring imparted by heat to colourless auriferous glass, the most probable, according to H. Rose (*Pogg.* 72, 556), is, that the colourless glass contains a silicate of aurous oxide, which requires a high temperature to produce it, and can bear that temperature without decomposition; but that when it is heated to a lower temperature, part of the aurous oxide separates out, and produces the colour; and finally, at a stronger heat, the separated aurous oxide is reduced, and the glass thereby rendered liver-coloured and opaque. Glass coloured by cuprous oxide exhibits precisely similar characters. ¶

## Gold and Tungsten.

A. Alloy of Gold and Tungsten. — Yellow; very refractory. (De Luyart.)

B. Auric Sulphotungstate. — $AuS^3, 3WS^3$. — Sulphotungstate of potassium forms with solution of chloride of gold a transparent, dark-brown mixture, which, when exposed to the air for a few days, forms a translucent precipitate, which blackens on being collected. (Berzelius.)

## Gold and Molybdenum.

A. Alloy of Gold and Molybdenum.—2 parts of gold and 1 part of molybdenum form a black, brittle globule. (Hielm.)

B. Molybdate of Auric Oxide, or Auric Molybdate.—Molybdate of potash added to a solution of chloride of gold, forms an orpiment-coloured precipitate, which is soluble in hydrochloric or nitric acid, and sparingly in water. (Richter.)

C. Auric Sulphomolybdate. — $AuS^3, 3MoS^3$. — The mixture of a normal solution of chloride of gold and sulphomolybdate of potassium, deposits, in the course of an hour, a dark brown powder, which becomes black on drying. (Berzelius, *Pogg.* 7, 277.)

D. Auric Persulphomolybdate.—$AuS^3, 3MoS^4$. — The precipitate formed by persulphomolybdate of potassium in a normal solution of chloride of gold, is of a dark brown colour. In drying, it undergoes partial decomposition, becoming yellow, and assuming somewhat of the metallic lustre; if it be then ignited in a retort, it gives off sulphur and becomes darker; and when subsequently heated in the air, burns away, evolving sulphurous acid, and forming a golden-yellow mixture of gold and molybdic acid, which sublimes at a stronger heat, and leaves the gold behind it. (Berzelius.)

Chromate of potash produces no precipitate in a solution of chloride of gold. (Thomson.)

## Gold and Manganese.

A. Alloy of Gold and Manganese.—By igniting gold with peroxide of manganese in a crucible lined with charcoal, a pale yellow, very hard alloy is formed, which is less fusible than gold, may be hammered flat to a slight extent before it breaks, has a coarse spongy fracture, and contains between $\frac{1}{9}$ and $\frac{1}{8}$ of manganese, which does not oxidate in the air till the alloy is fused. (Hatchett.)

B. Bromo-aurate of Manganese.—Dark brown, rhombic prisms, slightly translucent, with a reddish colour, and deliquescing rapidly in moist air. (Bonsdorff.)

C. Chloro-aurate of Manganese.—Yellow rhombic prisms, probably isomorphous with the magnesium-salt, permanent in dry winter air, but deliquescing in a summer atmosphere. (Bonsdorff.)

Permanganate of potash forms no precipitate with chloride of gold. (Fromherz.)

## Gold and Arsenic.

A. Arsenide of Gold.—Red-hot gold, exposed to the vapours of arsenic, fuses into a grey, brittle alloy, which is coarse-grained, easily fusible, and does not give off all its arsenic even when fused for two hours in an open crucible. (Hatchett.)

Arseniate of soda forms a yellowish white precipitate with solution of chloride of gold, on the application of heat. (Thomson.)

B. Auric Sulpharsenite.—The precipitate, which is yellow at first, but afterwards turns black, yields, when triturated after drying, a dark, yellowish brown powder; fuses readily in a retort; gives off a small quantity of orpiment at a dull red heat, but nevertheless remains liquid, and solidifies, on cooling, into a transparent, dark reddish yellow mass, which yields a dark brown powder, and is resolved at a white heat into volatile sulphide of arsenic and a residue of gold. (Berzelius.) The powder, when triturated for some time under water, assumes the lustre and colour of gold, although nothing is taken up by the water. (Berzelius.)

C. Auric Sulpharseniate.—*a.* $AuS^3,AsS^5$.—Formed by precipitating a solution of gold with terbasic sulpharseniate of sodium. Dark brown precipitate, soluble in pure water. Green vitriol decolorizes the solution, and throws down a yellowish brown substance.—*b.* $2AuS^3,3AsS^5$. By precipitation with $2NaS,AsS^5$.—Forms a red-brown solution in water. (Berzelius.)

## Gold and Antimony.

Antimonide of Gold.—Gold is easily fused with antimony; it likewise readily combines at a red heat with vapour of antimony.—An alloy of 9 parts of gold and 1 part of antimony is white, very brittle, and exhibits a fracture like that of porcelain. Gold loses its malleability by combination even with $\frac{1}{1920}$ of antimony. (Hatchett.) The antimony oxidizes and volatilizes, when the alloy is kept for some time in the fused state in contact with the air.

## Gold and Tellurium.

A. Telluride of Gold.—1. Precipitated on mixing a solution of chloride of gold with hydrotelluric acid or telluride of potassium.—2. Remains behind when B is heated. (Berzelius.)

Monotellurate of potash gives no precipitate with chloro-aurate of potassium. (Berzelius.)

B. Auric Sulphotellurite.—$AuS^3,TeS^2$.—A mixture of gold-solution and sulphotellurite of potassium is deep brown, opaque, and, after a few days, deposits the greater part of the compound in black voluminous flakes. The compound, when distilled, gives off dark-coloured sulphur, and leaves grey, brittle, easily fusible *telluride of gold*. (Berzelius.)

## Gold and Bismuth.

Alloy of Gold and Bismuth.—11 parts of gold form with 1 part of bismuth, a greenish yellow, very brittle compound, having a fine-grained

fracture, and a density of 18·038, consequently exhibiting condensation. Gold is rendered brittle by an admixture of $\frac{1}{1920}$ of bismuth. (Hatchett.)

¶ A native alloy of gold and bismuth, having a small quantity of mercury adhering to it, has been found among the washed gold from the works in Rutherford County, North America. It is in the form of small grains, having the colour of palladium. Sp. gr. from 12·4 to 12·9. Hardness 2·5 to 3; malleable, but ultimately becomes brittle. Structure [fracture?] indented. Fuses into a bead before the blowpipe, and crystallizes on cooling. When cupelled before the blowpipe, it yields a white fume, a yellow deposit, and a button of gold of about half the original size. (Shepard, *Sill. Am. J.* [2], 4, 280.) Shepard regards this alloy as a furnace-product; but Gibbon and Clingman consider it to be native, inasmuch as bismuth is of frequent occurrence in the southern States of North America. ¶

## Gold and Zinc.

A. Alloy of Gold and Zinc.—*a.* 60 pts. gold to 1 zinc: Brittle.—*b.* 11 gold to 1 zinc: Pale greenish yellow, brittle, of sp. gr. 16·937; hence there is condensation. (Hatchett.)—*c.* 1 pt. gold to 1 zinc: Very white and hard; capable of polish; does not oxidate readily in the air. (Hellat.)—*d.* 1 pt. gold to 2 zinc: Whiter than zinc; brittle; fine-grained. (Gehlen.)—*e.* 1 pt. gold to 7 zinc: According to Hellot, this alloy volatilizes completely at a strong heat.

B. Bromo-aurate of Zinc.—Dark brown-red prisms, which deliquesce rapidly even in rather dry air. (Bonsdorff.)

C. Chloro-aurate of Zinc.—The crystals, which are permanent in the air, have the same form and colour as those of chloro-aurate of magnesium. (Bonsdorff.)

## Gold and Cadmium.

Chloro-aurate of Cadmium.—Deep-yellow needles, permanent in the air. (Bonsdorff.)

A. Alloy of Gold and Tin.—Small quantities of tin impair the ductility of gold, but do not render it brittle. 11 parts of gold and 1 part of tin form a very pale yellow, slightly malleable alloy, having a fine-grained fracture, and a specific gravity of 17·307, and therefore exhibiting condensation. The separation of the two metals is very difficult, but is best effected by fusion with sulphide of antimony. (Hatchett.) When solutions of chloride of gold and protochloride of tin are mixed, both being concentrated and the latter in excess, an alloy of gold and tin is precipitated in the form of a black-brown powder, which acquires the metallic lustre and a pale yellow colour under the burnishing-steel, and when melted yields a white, brittle globule. (Berzelius.)

B. Stannate of Aurous Oxide.—*Gold-purple, Purple of Cassius, Purpura mineralis Cassii.*

*Formation.* 1. By mixing a solution of chloride of gold with the solution of a stannous salt.—Pure protochloride of tin forms with chloride

of gold, when tolerably concentrated, a brown precipitate, consisting of an alloy of the two metals; it is only in case of very great dilution that the purple is produced. (Berzelius.)—A very dilute solution of protochloride of tin likewise forms with gold-solution, not the purple, but a black-brown opaque mixture, probably containing an alloy of tin and gold; but this mixture, when kept in an open vessel, turns red from above downwards, and slowly deposits a very fine purple, which, however, is not always soluble in ammonia. (Fuchs.)—The brown powder is formed only with an excess of tin-solution; when the gold solution is in excess, pure gold is precipitated. (Oberkampf.)—When both liquids are as neutral as possible, or when the chloride of tin is in excess, metallic gold is precipitated, exhibiting a brown, blue, or green colour; and on heating this precipitate with excess of gold-solution, it is slowly converted into purple of Cassius; if, however, nitric acid be present, the purple may be produced by its oxidizing action. (Buisson.) The colour of the purple is bright red when a small quantity of tin-solution is used, and violet when the quantity of the latter is larger. (Oberkampf.) It is violet when an excess of bichloride of tin is present. (Buisson.) If the tin-solution contains more protoxide than bioxide of tin, or if it is not sufficiently diluted, a dark-coloured, nearly black precipitate is produced, which also dissolves in ammonia while yet moist, but forms a perfectly brown solution; after drying, it is black, gives off water when ignited, and leaves a brick-red mixture of gold and stannic oxide. (Berzelius.)—If the solution of protochloride of tin contains a very large excess of acid, metallic gold is precipitated instead of the purple.—Stannous sulphate likewise forms the purple with gold-solution (Proust), but only after a considerable time (Sarzeau).—Stannous nitrate yields, under all circumstances, even with concentrated solutions, a beautiful purple. (Fischer, *Schw.* 56, 363.)—Metallic tin, tin-foil, for example, likewise throws down purple of Cassius from an acid solution of chloride of gold.—Bichloride of tin gives no precipitate with gold-solution. (Proust.) Potash added to the mixture forms a brown precipitate, which retains its colour when dry; when heated under the liquid, it is converted into a brick-red mixture of gold, tin, and stannic oxide, which exhibits a conchoidal fracture when dry. (Berzelius.)—The purple of Cassius is not formed by pouring a solution of bichloride of tin on protochloride of gold. (Schweigger-Seidel, *Schw.* 62, 265.)

2. By pouring a solution of chloride of gold on hydrated sesquioxide of tin. If the action be too long continued, the purple decomposes again, especially if the gold-solution is not dilute, part of the gold being reduced to the metallic state, and the rest dissolving in the form of auric oxide, together with the stannic oxide, in the hydrochloric acid. (Fuchs, *Kastn. Arch.* 23, 368.)

3. By boiling protoxide of gold with aqueous stannate of potash. (Figuier.)

4. By the action of oxidizing agents on metallic alloys containing gold and tin. When an alloy of 500 pts. silver, 1 gold, and 25 tin is dissolved in nitric acid, 32·5 pts. of a pale red gold-purple are formed, in consequence of the excess of stannic oxide. Formation of purple likewise takes place when auriferous silver is dissolved in gently heated nitric acid, and metallic tin is added during the solution: stannic oxide has no action. Alloys of gold with tin, or with tin and zinc together, yield the purple when dissolved in nitric acid, the colour being particularly fine in the case of the alloy of tin and zinc; on dissolving these alloys in hydro-

chloric acid, on the contrary, metallic gold separates out. (Mercadieu, *Ann. Chim. Phys.* 34, 147; also *N. Tr.* 15, 2, 30.) An alloy of 1500 pts. silver, 200 gold, and 350·5 tin (fused together under borax to prevent all oxidation of the tin) yields, by solution in nitric acid, a quantity of gold-purple, which weighs 701 parts when dried at 100°, and at a red heat gives off 53 parts of water, with a trace of hyponitric acid. Hence the composition calculated further on. The gold-purple thus obtained from alloys by nitric acid appears homogeneous, but is denser than the ordinary variety, its density being greater, the smaller the quantity of silver that was present in the alloy; it is likewise insoluble in ammonia. (Gay-Lussac, *Ann. Chim. Phys.* 34, 396.) 100 parts of filings of an alloy of 1 part of gold and 99 of copper, intimately mixed with 3·5 parts of tin, yields no purple with nitric acid, and a very dingy product with boiling oil of vitriol. An intimate mixture of tin, gold, and a large quantity of silver, or of 2 pts. gold, 7 tin, and 900 sugar or phosphate of lime, yields no purple when treated with nitric acid. Neither is the purple produced by heating auriferous copper with a solution of tin in boiling oil of vitriol, whereby the copper is dissolved, and the gold separated in the metallic state. (Sarzeau.) Some very much corroded coins of the Roman empire dug out of the ground in France, yield cupric oxide to aqueous ammonia when triturated with that liquid; the undissolved portion consists of two powders of different densities, which may be separated by levigation. The lighter powder, which has a dingy red colour, is a mixture of silver spangles and purple of Cassius (containing metallic gold and tin), which assumes a purple-red colour after the silver has been dissolved out by nitric acid; but the colour is often dingy from admixture of sulphide of silver. When the filings of the better preserved coins are repeatedly moistened with acetic acid and exposed to the air, and the resulting cupric acetate dissolved out by water, there likewise remains a mixture of silver-spangles and gold-purple, which, when freed by nitric acid from silver, and by hydrochloric acid from the iron of the file, exhibits a fine colour. (Sarzeau, *N. J. Pharm.* 3, 373.)

*Preparation.*—1. By mixing aqueous sesquichloride of iron with aqueous protochloride of tin till the yellow colour is converted into pale green, and precipitating the gold-solution with the mixture thus formed. (Fuchs, *J. pr. Chem.* 5, 318.) This process yields the finest purple; the protochloride of iron contained in the liquid does not affect the product. (Fuchs.) One part of the *Liquor ferri muriatici* of the *Pharmac. Bor.* is mixed with 3 parts of water, and a solution of 1 pt. tin-salt in 6 pts. water added, till the mixture acquires a greenish tint, after which 6 pts. more of water are added. (If the water were added at first, the change of the brownish into the greenish tint could not be so well observed.) On the other hand, gold is dissolved in boiling hydrochloric acid, with gradual addition of nitric acid—care being taken, however, to avoid as much as possible an excess of acid, especially of the nitric acid; the solution is diluted so far that 360 parts of the liquid contain 1 part of gold: and the tin-solution is then added, with constant stirring, as long as a precipitate is produced. By this process, 100 parts of gold yield 360 parts of dried purple, soluble in ammonia, and capable of imparting a strong colour to glass. If the gold-solution contains only 1 part of gold in 450, instead of 360 parts of the liquid, a good purple is likewise obtained at temperatures between 30° and 35°; but at ordinary temperatures, it is not deposited; and on heating the liquid to the boiling point, it

falls down in red-brown flakes, which are not soluble in ammonia, and imparts but a slight colour to glass. (Capaun, *J. pr. Chem.* 22, 152.)—2. Ten parts of pink-salt (V, 94) are heated with 1·07 tin-foil and 40 water, till the tin is dissolved, after which 140 parts of water are added:

$$3(NH^4Cl,SnCl^2) + Sn = 3NH^4Cl + 2Sn^2Cl^3.$$

On the other hand, 1·34 pt. gold is dissolved in aqua-regia, the acid not being in excess, and a quantity of water is added, sufficient to bring the mixture up to 480 parts. Finally, the former solution is added to the latter slightly warmed, as long as a precipitate is produced. The purple, which is quickly deposited, weighs 4·92 parts, after washing and drying at 100°; the filtrate has a very pale red colour. (Bolley, *Ann. Pharm.* 39, 244.)—3. *a.* A neutral solution is prepared of 1 part of tin in hydrochloric acid; *b.* a solution of 2 pts. tin in cold nitro-hydrochloric acid (1 pt. hydrochloric acid to 3 nitric), the liquid being merely heated, if necessary, towards the end of the process, so that the solution may not contain any protoxide of tin, and therefore may not precipitate the gold-solution; *c.* 7 parts of gold are dissolved in nitro-hydrochloric acid (6 hydrochloric to 1 nitric), and the solution, which is tolerably neutral, diluted with 3500 parts of water. To this solution *c* the solution *b* is first added, and then the solution *a*, drop by drop, till the right colour is produced. If the quantity of *a* be too small, the precipitate is violet; if too large, it is brown. It must be washed quickly, so that the liquid may not act too long upon it. If the precipitate will not settle down, the mixture must be slowly poured into a glass of water, so that it may sink to the bottom, and the two liquids may mix but slowly. (Buisson, *J. Pharm.* 16, 629.) The purple thus obtained weighs only 6·2 pts.; it dissolves in ammonia while fresh, but imparts a scarcely perceptible colour to glass-fluxes; the filtrate is red; but deposits no more purple on the further addition of protochloride of tin. (Capaun).—Lentin (*Scher. J.* 3, 30) drops fuming nitric acid into aqueous protochloride of tin, till a sample of the mixture forms a fine purple with the gold-solution, and then mixes the liquids.—4. To obtain a *blue precipitate*, a solution (*a*) as neutral as possible, of 3 grammes of tin in hydrochloric acid, is prepared out of contact of air, and (*b*) a solution as neutral as possible of 3 grammes of gold in aqua-regia; each of these solutions is diluted with a litre of water; 10 measures of solution *a* are heated to between 50° and 60° with 3 measures of nitric acid; 1 measure of *b* is then added, and immediately afterwards water, with agitation. The indigo-blue precipitate (or violet, if sufficient water has not been added), must be quickly washed by decantation, as, if left for any length of time under the liquid in an open vessel, it changes colour first to violet and then to purple. (Golfier Besseyre, *Ann. Chim. Phys.* 54, 40; also *J. pr. Chem.* 20, 65.)

*Properties.*—In the moist state, dark purple-red (dark brown, according to Berzelius). Brown after drying. (Capaun, Bolley.)

| | Proust. | Berzelius. | Buisson. | Gay-Lussac. | Oberkampf. *violet.* | Oberkampf. *purple.* |
|---|---|---|---|---|---|---|
| Au | 24 | 28·2 | 28·5 | 28·53 | 39·82 | 79·42 |
| $SnO^2$ | 76 | 64·0 | 65 9 | 63·56 | 60·18 | 20·58 |
| HO | | 7·6 | | 7·56 | | |
| Cl | | | 5·2 | $NO^5$ trace. | | |
| | 100 | 99·8 | 99·6 | 99·65 | 100·00 | 100·00 |

The purple examined by Proust was obtained with gold-solution and aqueous protochloride of tin, and well dried; that examined by Berzelius was obtained with very weak solutions of terchloride of gold and proto-

chloride of tin. Buisson's purple was prepared by (3); if the tin-solution contains too much nitric acid, basic nitrate of stannic oxide is precipitated, instead of the stannic oxychloride. Buisson does not appear to have looked for water, and his amount of chlorine is doubtful, since, according to Berzelius, the purple neither gives off hydrochloric acid nor chloride of tin when ignited. Gay-Lussac's purple is the product obtained from the alloy of gold and tin by the action of nitric acid, and dried at 100°. Oberkampf's violet purple was obtained by precipitating the gold-solution with excess of tin-solution; in the preparation of his purple product, the gold-solution was in excess. The analyses are partly incorrect, for this reason, that if an excess of stannic salt is present, an excess of stannic oxide is precipitated; and if the stannous salt is in excess, the brown alloy of gold and tin mixes with the precipitate.

The following are the principal theories which have been put forward regarding the composition of gold-purple:—I. *It contains metallic gold with hydrated stannic oxide* (or, according to Buisson, with stannic oxychloride).—1. The two substances are mechanically mixed; the very finely divided gold is the colouring principle, and the stannic oxide assists by its interposition the development of the colour, in the same manner as alum in the colours called *lakes*. (Buisson, Sarzeau.) [In that case, an excess of stannic oxide would merely weaken the purple colour, but could not change it into violet; moreover, in lakes, the alum is chemically combined with the colouring principle.]—2. The gold is chemically combined with the stannic oxide. (Proust.) Gay-Lussac likewise supposes a combination by affinity, or at least by intimate adhesion.—II. *The purple of Cassius contains oxidized gold.* This view is the more probable of the two.—1. It contains protoxide of gold. Purple of Cassius, freed by potash from excess of stannic oxide, has the composition: $AuO,3SnO^2+4Aq$. (*see* Calculation *a*). This is exactly the composition of the gold-purple obtained by boiling protoxide of gold with stannate of potash, or by immersing tin-foil in the solution of chloride of gold; and the gold-purple analyzed by Berzelius contains exactly the double quantity of stannic acid = $AuO,6SnO^2+7Aq$. (Figuier.) [6Aq. is nearer; *vide* Calculation *b*; but Figuier's view is in opposition to the observation made by Berzelius, that the purple gives off no oxygen when ignited.] Schweigger-Seidel (*Schw.* 65, 265) regards the purple of Cassius as stannate of aurous oxide and stannous oxide = $SnO,3SnO^2+AuO,2SnO^2+6Aq$.—2. The purple of Cassius contains a purple oxide of gold = $AuO^2$, intermediate between the protoxide and teroxide. (Berzelius, Fuchs, Desmarest.) It is composed of $AuO^2,2Sn^2O^3$ [perhaps also with 4 At. water? *see* Calculation *c*]. This formula agrees with Oberkampf's analyses of the violet gold-purple. (Berzelius.) [But this is not the true gold-purple.] Its formula is: $2(SnO,SnO^2)+AuO^2,2SnO^2+6Aq$. (Calculation *d*). Fuchs (*Pogg.* 27, 634). The formation of gold-purple from a mixture of hydrochlorate of auric oxide and hydrochlorate of sesquioxide of tin would accordingly take place as follows:

$$AuO^3,3HCl+3(Sn^2O^3,3HCl)=[2(SnO,SnO^2)+AuO^2,2SnO^2]+12HCl.$$

*Calculations according to the preceding hypotheses.*

| | At. | Figuier, *a*. | At. | Figuier, *b*. | At. | Berzelius, *c*. | At. | Fuchs, *d*. |
|---|---|---|---|---|---|---|---|---|
| Au | 1 | 199 | 42·51 | 1 | 199 | 27·99 | 1 | 199 | 37·20 | 1 | 199 | 28·31 |
| Sn | 3 | 177 | 37·82 | 6 | 354 | 49·79 | 4 | 236 | 44·11 | 6 | 354 | 50·35 |
| O | 7 | 56 | 11·97 | 13 | 104 | 14·62 | 8 | 64 | 11·96 | 12 | 96 | 13·66 |
| HO | 4 | 36 | 7·70 | 6 | 54 | 7·60 | 4 | 36 | 6·73 | 6 | 54 | 7·68 |
| | | 468 | 100·00 | | 711 | 100·00 | | 535 | 100·00 | | 703 | 100·00 |

*Decompositions.*—Purple of Cassius retains its water when heated above 100°, but gives it up at a red heat, without at the same time emitting any permanent gas, and acquires a brick-red colour. (Berzelius.) Aqua-regia dissolves out the gold from the ignited residue, leaving white stannic oxide. (Proust, Berzelius.) Hydrochloric acid has no action upon it. (Berzelius.) Berzelius regards ignited gold-purple as a mixture of gold and stannic oxide, inasmuch as, at a red heat, the red oxide of gold gives up its oxygen to the sesquioxide of tin, and forms bioxide of tin; for an intimate mixture of oxide of gold with a large quantity of sulphate of potash likewise forms, when ignited, a red powder, from which water extracts the salt, and leaves metallic gold. According to Fuchs, the ignited purple is only to be regarded as de-hydrated, for mercury does not dissolve gold from it; the affinity of the stannic acid for the red oxide of gold prevents the decomposition. Gold-purple fused with nitre yields stannate of potash and a white globule of an alloy of gold and tin. (Berzelius.) It is but slightly altered by red-hot fusion with bisulphate of potash. It likewise remains unaltered when fused with carbonate of potash, and does not expel carbonic acid from that salt. (Berzelius.) [This fact is in favour of Fuchs's theory, that ignited gold-purple still contains stannic acid in the combined state.] Gold-purple is blackened by protochloride of tin and other deoxidizing liquids. (Desmarest, *J. Pharm.* 17, 219.) Aqua-regia extracts from the unignited purple all the gold, together with a small quantity of tin, leaving the greater part of the stannic oxide undissolved. (Proust.) This liquid dissolves the purple easily, at first with a violet colour. (Buisson.) Hydrochloric acid acts upon it slowly, dissolving up all the tin, after long boiling, in the form of bioxide, free from protoxide, and leaving all the gold in the metallic state. (Proust, Fuchs.) [This action favours the views of Fuchs and Berzelius, and is against that of Figuier]. Boiling nitric acid brightens the colour of recently prepared gold-purple, and dissolves out some of the stannic oxide, together with a small quantity of auric oxide. (Proust.) Boiling dilute sulphuric acid likewise heightens the colour, and extracts a small quantity of stannic oxide. (Proust.) The purple while moist is not decomposed by long boiling with water, merely falling more quickly to the bottom. (Robiquet.) Boiling potash has likewise no action on the moist purple. (Berzelius.) It dissolves out the excess of stannic oxide. (Figuier.) Mercury does not extract gold from recently prepared gold-purple (Proust); not even with the aid of heat or sunshine; neither does it dissolve gold out of the ignited purple. (Fuchs.) At temperatures between 100° and 150°, it dissolves out all the gold from the dried and pulverized purple, and leaves stannic oxide. (Buisson.) At this temperature, the mercury may exert a reducing action on the red oxide of gold. (Berzelius.) Gold-purple fused with 4 parts of lead-oxide and 1 part of borax, yields a violet glass on the addition of a large quantity of boracic acid, and a red glass on the addition of a large quantity of hydrate of potash.

Gold-purple, while yet moist, dissolves in aqueous ammonia, forming a deep purple-red liquid, from which the purple separates both on evaporation and on the addition of acids, but not on dilution with water, unless the quantity dissolved is excessive. (Proust.) After drying, the purple is no longer soluble. (Berzelius.) The solubility of the moist purple is also destroyed by allowing it to freeze. (Fuchs.) The purple obtained by treating the hydrated sesquioxide of tin with solution of chloride of gold (Fuchs), and that produced on dissolving an alloy of

gold, silver, and tin in nitric acid (Gay-Lussac), are not soluble in ammonia, even while moist, the insolubility probably arising from their greater density.—The solution, when not completely saturated, is quite clear; but a perfectly saturated solution, though it appears clear by transmitted light, nevertheless exhibits some degree of turbidity when viewed by reflected light. The solution, when left in the dark for some weeks, becomes decolorized from above downwards, while gelatinous gold-purple, mixed with metallic gold, falls to the bottom; on agitation, a red liquid is again obtained—which, however, quickly deposits the purple again—and after a while, metallic gold is precipitated, the quantity continually increasing. When the ammoniacal solution is kept in a stoppered bottle at temperatures between 60° and 80°, the purple is more quickly deposited, and is not re-dissolved on agitation. On evaporating the solution at a gentle heat, the purple separates in the form of a jelly, no longer soluble in ammonia, but otherwise unaltered. (Berzelius, *Lehrbuch.*) The ammoniacal solution of gold-purple turns violet when exposed to light, and gradually deposits the whole of the gold in the metallic state, the transparent and colourless liquid containing ammonia free from stannous oxide. (Fuchs.)

## Gold and Lead.

A. Alloy of Gold and Lead.—11 parts of gold and 1 part of lead form a pale yellow alloy, as brittle as glass, having a fine-grained fracture, and a density of 18·08, less therefore than the mean. The ductility of gold is destroyed by admixture of $\frac{1}{1920}$ of lead. (Hatchett.) The lead oxidates when the compound is fused in the air.

B. Telluride of Lead and Gold?—*Foliated Tellurium.*—Crystalline system, the square prismatic. *Fig.* 23, 27, 28, 30, 32, 33, and other forms. Specific gravity, 6·84 (Berthier); 7·22 (Petz). Soft and sectile, with a strong lustre and dark lead-grey colour; yields a powder of the same colour. Fuses very readily before the blowpipe, fuming, imparting a blue colour to the flame, and depositing a yellow film on the charcoal; after continued blowing, it yields a globule of gold. Dissolves in nitric acid, leaving a residue of sulphur and chloride of lead.—The want of accordance in the analyses, probably arising from admixture of other tellurium ores and sulphide of lead, renders it impossible to deduce any definite formula for the mineral.

| | Klaproth. | | Brandes. | | Berthier. | | Petz. |
|---|---|---|---|---|---|---|---|
| Pb | 54·0 | .... | 55·49 | .... | 63·1 | | |
| Cu | 1·3 | .... | 1·14 | .... | 1·0 | | |
| Ag | 0·5 | .... | trace | | | | |
| Au | 9·0 | .... | 8·44 | .... | 6·7 | .... | 6·18 to 8·51 |
| Te | 32·2 | .... | 31·86 | .... | 13·0 | | |
| Sb | | .... | | .... | 4·5 | | |
| S | 3·0 | .... | 3·07 | .... | 11·7 | | |
| | 100·00 | .... | 100·00 | .... | 100·0 | | |

## Gold and Iron.

A. Alloy of Gold and Iron.—*a.* 11 parts of gold to 1 part of iron; Yellowish-grey, very extensible, hard; sp. gr. 16·885,—less than the mean.—*b.* 1 pt. gold to 1 pt. iron; Grey.—*c.* 1 pt. gold to 4 iron; Silver-white. (Lewis.)

B. Carbide of Gold and Iron.—Gold does not improve the quality of steel; the presence of more than 4 per cent. of gold makes it brittle. (Bréant.)

C. Iodo-aurate of Iron.—Aqueous iodide of iron dissolves a large quantity of teriodide of gold, and yields a crystallizable compound. (Johnston.)

### Gold and Cobalt.

A. Alloy of Gold and Cobalt.—18 parts of gold form, with 1 part of cobalt, a dark yellow, very brittle compound, having an earthy, light yellow fracture. An alloy containing $\frac{1}{65}$ of cobalt is still brittle; $\frac{1}{110}$ of cobalt gives a malleable compound. (Hatchett.)

B. Chloride of Gold and Cobalt.—By spontaneous evaporation of an aqueous mixture of teriodide of gold and protochloride of cobalt, long rhombic prisms are obtained, having a deep yellow colour, and permanent in the air. (Bonsdorff.)

### Gold and Nickel.

A. Alloy of Gold and Nickel.—The two metals unite with facility, forming a yellowish-white, hard, very malleable alloy, susceptible of a high polish, and having a magnetic power as great as that of nickel. (Lampadius, *Schw.* 10, 176.)

B. Chloride of Gold and Nickel.—Short greenish yellow prisms, isomorphous with those of the corresponding magnesium-salt. (Bonsdorff.)

### Gold and Copper.

A. Alloy of Gold and Copper.—*Rothe Karatirung.*—In alloys of gold, the mark is divided into 24 carats, and the carat into 12 grains. Accordingly, perfectly pure gold is said to be *twenty-four carats fine*, and an alloy containing 18 carats of gold and 6 carats of copper or silver (or both together) is said to be *eighteen carats fine*, &c. The addition of copper renders gold redder, harder, and more fusible. Pure copper produces but little diminution in the malleability of gold; but copper containing lead or antimony makes it brittle. An alloy containing 22 parts of gold and 1 part of copper has a density of 17·157; according to Muschenbroek, the maximum of hardness is exhibited by an alloy of 7 pts. gold and 1 copper. The copper cannot be completely separated from the alloy by fusion in contact with the air, nor even by cupellation with a large quantity of lead; it is only when a triple weight of silver and a twenty-four-fold weight of lead are simultaneously added to the alloy of gold and copper, that the whole of the copper sinks into the cupel, in the form of a compound of cupric oxide and lead-oxide. According to Macculloch, the copper may be superficially dissolved out of the alloy by heated aqueous ammonia; and by the same means, the alloy may be cleaned when it has become tarnished by oxidation of the copper.

B. Alloy of Gold, Copper, and Zinc.—Gold forms with brass a brittle, coarse-grained alloy. (Hatchett.)

## Gold and Mercury.

Amalgam of Gold.—Formed even at ordinary temperatures; most quickly, however, by throwing red-hot gold-plate into heated mercury. A bar of gold dipped into cold mercury, quickly turns white, and is soon completely penetrated by the mercury; but even after the lapse of a month, it still remains malleable, and is covered with small crystals. When the mercury is heated to the boiling point, it soon dissolves, and forms a pasty amalgam. (Daniell.) Yellowish white; the amalgam containing 6 pts. mercury and 1 gold crystallizes in four-sided prisms, which are fusible at a high temperature. If the mercury be carefully distilled off, the gold remains in an arborescent form.—Serves for *gilding by heat.* The amalgam obtained by dipping a red-hot gold-plate into hot mercury is triturated in a stone-ware mortar with salt and water, till it becomes perfectly bright, and then freed from excess of mercury by pressure through chamois-leather.

¶ A native amalgam of gold has been found in Columbia, associated with a platinum ore, in globules of the size of a pea, and easily crushed by pressure. It gave by analysis 57·40 per cent. Hg; 38·39 Au; 5·0 Ag $= \left.\begin{matrix}\mathrm{Au}\\ \mathrm{Ag}\end{matrix}\right\}^{5} \mathrm{Hg}^{12}$. (Schneider, *J. pr. Chem.* 43, 317.) ¶

## Gold and Silver.

A. Alloy of Gold and Silver. — Found native in the forms of *Auriferous Silver* and *Electrum.*—The alloy is also formed artificially (*Weisse Karatirung.*)—Gold, by combination with silver, becomes harder, more sonorous, and more fusible; and as the proportion of silver increases, the colour quickly passes through pale greenish yellow into white: the alloy exhibits a slight degree of expansion. The malleability of gold is less diminished by silver than by any other metal. The maximum of hardness is found in the alloy containing 2 pts. of gold to 1 of silver. (Muschenbroek.) An alloy of 1 pt. gold and from 3 to 4 pts. silver, spits when suddenly cooled after fusion (p. 137). (G. Rose, *Pogg.* 23, 181.) —[For the separation of the two metals, see pp. 201—204.]

When gold-powder and silver-powder are welded together by Wollaston's process for platinum, a damasked metal is obtained; but at the points of contact of the gold and silver, an alloy is formed; the metals are therefore capable of uniting at temperatures far below their melting points. (Tournet, *Ann. Chim. Phys.* 75, 435.)

The native alloy of *Gold and Silver* exhibits the crystalline forms of the two metals, and a very variable proportion of them; and accordingly presents great diversity of specific gravity and colour. The assumption of definite stoïchiometrical proportions, to which Boussingault was led by his analyses of Columbian ores (*Ann. Chim. Phys.* 34, 408; 45, 440), has been shown by the more elaborate analyses of Gustav Rose to be inadmissible. Here follow the analyses, beginning with those of nearly pure native gold. [Those marked with a star are added by the translator.]

| | *a.* | *b.** | *c.* | *d.* | *e.* | *f.* | *g.* |
|---|---|---|---|---|---|---|---|
| Au | 98·96 | 98·3 | 98 | 95·33 | 95·30 | 94·41 | 94·09 |
| Ag | 0·16 | 1·7 | 2 | 4·34 | 3·86 | 5·23 | 5·55 |
| Cu | 0·35 | | | | | | |
| Fe | 0·05 | | | 0·33 | 0·84 | 0·36 | 0·36 |
| | 99·52 | 100·0 | 100 | 100·00 | 100·00 | 100·00 | 100·00 |

*a.* From the gold-sand of Schabrowski, near Katharinenburg; sp. gr. 19·099; after fusion 19·10. (Rose.)—*b.* Locality unknown. (Levol, *N. Ann. Chim. Phys.* 27, 310.)—*c.* From Bucaramanga. (Boussingault.)—*d.* From the Ural, in rhombic dodecahedrons, of sp. gr. 18·791, after fusion. (Awdejew, *Pogg.* 53, 153.)—*e.* From the Ural; dodecahedrons; sp. gr. 18·771, before fusion; 18·892, after fusion. (Awdejew.)—*f.* From the gold-sand of Boruschka, near Nischne-Tagil; sp. gr. 18·44. (Rose.)—*g.* From the Ural; dodecahedrons. (Awdejew.)

| | *h.** | *i.* | *k.* | *l.* | *m.* | *n.* | *o.** |
|---|---|---|---|---|---|---|---|
| Au | 94·00 | 93·78 | 93·75 | 93·66 | 93·54 | 93·34 | 93·0 |
| Ag | 5·85 | 5·94 | 6·01 | 5·72 | 5·62 | 6·28 | 6·7 |
| Cu | | 0·08 | 0·24 | 0·52 | 0·80 | 0·06 | |
| Fe | | 0·04 | | | | 0·32 | |
| Pt | 0·15 | | | | | | |
| | 100·00 | 99·84 | 100·00 | 99·90 | 99·96 | 100·00 | 99·7 |

*h.* From Senegal. (Levol.)—*i.* From Beresow. (Rose.)—*k*, *l*, and *m.* From the Ural; dodecahedrons. (Awdejew.)—*n.* From Katharinenburg. (Rose.)—*o.* From California; sp. gr. 16·23. (Rivot, *Ann. Min.* [4], 16, 127.)

| | *p.** | *q.* | *r.* | *s.** | *t.* | *u.* | *v.** |
|---|---|---|---|---|---|---|---|
| Au | 93 | 92·80 | 92·71 | 92·7 | 92·60 | 92·47 | 92·32 |
| Ag | 7 | 7·02 | 6·51 | 6·9 | 7·08 | 7·27 | 6·17 |
| Cu | | 0·06 | 0·78 | 0·4 | 0·02 | 0·18 | |
| Fe | | 0·08 | | | 0·06 | 0·08 | 0·78 |
| | 100 | 99·96 | 100·00 | 100·0 | 99·76 | 100·00 | 99·27 |

*p.* From California; sp. gr. 16·33; this sample contained 1·66 per cent. of sand and oxide of iron, mechanically mixed with it. (Teschemacher, *Chem. Soc. Qu. J.* 2, 193.)—*q.* From Katharinenburg. (Rose.)—*r.* From the Ural; dodecahedrons; sp. gr. 18·11; increased by fusion to 18·399. (Awdejew.)—*s.* From California. (Levol.)—*t.* From the gold-sand of Pawlowsk, near Beresow. (Rose.)—*u.* From the gold-sand of Nikolajewsk, near Minsk. (Rose.)—*v.* From the river-sand of the county of Wicklow, in Ireland; sp. gr. 16·34 (Mallet, *Phil. Mag. J.* 37, 393.)

| | *a.* | *b.* | *c.* | *d.** | *e.* | *f.* | *g.** |
|---|---|---|---|---|---|---|---|
| Au | 92·01 | 91·9 | 91·88 | 91·4 | 91·36 | 91·21 | 91·0 |
| Ag | 7·52 | 8·1 | 8·03 | 8·5 | 8·35 | 8·03 | 8·7 |
| Cu | 0·30 | | 0·09 | | 0·29 | 0·76 | 0·3 |
| Fe | 0·17 | | trace | | | | |
| | 100·00 | 100·0 | 100·00 | 99·9 | 100·00 | 100·00 | 100·0 |

*a.* From Bucharia. (Rose.)—*b.* This is probably the composition of the electrum from Quiebralmo; also of that from Giron. (Boussingault.)—*c.* From Beresow. (Rose.)—*d.* From California; sp. gr. 16·65. (Rivot.)—*e.* From the gold-sand of Boruschka; sp. gr. 17·955, increasing by fusion to 17·965. (Rose.)—*f.* From the Ural; dodecahedrons; sp. gr. 17·74; after fusion, 18·35. (Awdejew.)—*g.* From the North of Brazil. (Levol.)

| | *h.** | *i.** | *k.* | *l.** | *m.** | *n.* | *o.** |
|---|---|---|---|---|---|---|---|
| Au | 90·96 | 90·9 | 90·76 | 90·12 | 89·61 | 89·35 | 89·1 |
| Ag | 9·04 | 8·7 | 9·02 | 9·01 | 10·05 | 10·65 | 10·5 |
| Cu | | | 0·22 | 0·87 | | trace | |
| Fe | | 0·2 | | | | trace | 0·2 |
| | 100·00 | 99·8 | 100·00 | 100·00 | 99·66 | 100·00 | 99·8 |

*h.* From California; after deduction of 3·7 per cent. of sand. (Oswald,

*Pogg.* 78, 96.)—*i.* From California; sp. gr. 51·7. (Rivot.)—*k.* From Boruschka; sp. gr. 17·588; after fusion, 17·745. (Rose.)—*l.* From California. (Henry, *Phil. Mag. J.* 34, 205.)—*m.* From California. (Hofmann, *Ann. Pharm.* 70, 255.)—*n.* From the gold-sand of Nikolajewsk; sp. gr. 17·484; after fusion, 17·725. (Rose.)—*o.* From California; sp. gr. 17·55. (Rivot.)

| | *p.* | *q.* | *r.* | *s.* | *t.* | *u.* | *v.* |
|---|---|---|---|---|---|---|---|
| Au | 88·65 | 88·58 | 88·24 | 88·15 | 87·40 | 87·94 | 87·31 |
| Ag | 10·64 | 11·42 | 11·76 | 11·85 | 12·07 | 12·06 | 12·12 |
| Cu | 0·09 | | | | 0·09 | | 0·08 |
| Fe | 0·35 | | | | trace | | 0·24 |
| | 99·73 | 100·00 | 100·00 | 100·00 | 99·56 | 100·00 | 99·75 |

*p.* From the Newinsk mine.—*q.* From Llano. (Boussingault.)—*r.* From Malpeso; sp. gr. 14·706 [?]. (Boussingault.)—*s.* From Baja, near Pamplona. (Boussingault.)—*t.* From the gold-sand of Andrejewski, near Miask; sp. gr. 17·402; after fusion, 17·542. (Rose.)—*u.* From Rio Sucio; sp. gr. 14·690 [?]. (Boussingault.)—*v.* From Gazuschka, near Nischne Tagil. (Rose.)

| | *a.** | *b.** | *c.* | *d.* | *e.* | *f.** | *g.* |
|---|---|---|---|---|---|---|---|
| Au | 86·8 | 86·57 | 86·10 | 84·89 | 84·5 | 84·5 | 83·85 |
| Ag | 11·3 | 12·33 | 13·19 | 14·68 | 15·5 | 15·3 | 16·15 |
| Cu | 0·9 | 0·29 | trace | 0·04 | | | trace |
| Fe | | 0·24 | | 0·13 | | | trace |
| | 99·0 | 99·43 | 99·29 | 99·74 | 100·0 | 99·8 | 100·00 |

*a.* Gold-laminæ, from Senegal. (Levol.)—*b.* From California; sp. gr. 15·63. (Henry.)—*c.* From the gold-sand of Petropawlowsk, near Bogoslowsk; sp. gr. 16·896; after fusion, 16·964. (Rose.)—*d.* From the St. Barbara mine at Füses, in Transylvania. (Rose.)—*e.* From Ojas Ancas. (Boussingault.)—*f.* Gold-dust from Senegal. (Levol.)—*g.* From the gold-sand of Boruschka; sp. gr. 17·061. (Rose.)

| | *h.* | *i.* | *k.* | *l.* | *m.* | *n.* | *o.* |
|---|---|---|---|---|---|---|---|
| Au | 82·4 | 82·1 | 79·00 | 76·41 | 74·4 | 74 | 73·68 |
| Ag | 17 6 | 17·9 | 20·34 | 23·12 | 25·6 | 26 | 26·32 |
| Cu | | | 0·66 | 0·03 | | | |
| Fe | | | | trace | | | |
| | 100·0 | 100·0 | 100·00 | 99·56 | 100·0 | 100 | 100·00 |

*h.* From Trinidad, near Sta. Rosa de Osos. (Boussingault.)—*i.* From Vega de Sapia. (Boussingault.)—*k.* From the Ural; tetrahedrons; sp. gr. after hammering, 16·03. (Awdejew.)—*l.* From Titiribi, in Columbia. (Rose.)—*m.* From the Sebastian mine at Marmoto. Crystals of a brass-yellow colour. (Boussingault.)—*n.* From Titiribi. (Boussingault.)—*o.* From Guamo. (Boussingault.)

| | *p.* | *q.* | *r.* | *s.* | *t.* | *u.* | *v.* | *w.* | *x.* |
|---|---|---|---|---|---|---|---|---|---|
| Au | 73·45 | 73·4 | 70·86 | 64·93 | 64·52 | 64 | 60·98 | 60·49 | 28 |
| Ag | 26·48 | 26·6 | 28·30 | 35·07 | 35·48 | 36 | 38·38 | 38·74 | 72 |
| Cu | | | 0·84 | | | | — | 0·77 | |
| Fe | | | | | | | 0·33 | | |
| | 99·93 | 100·0 | 100·00 | 100·00 | 100·00 | 100 | 99·69 | 100·00 | 100 |

*p.* From Marmato; cubes and octohedrons of specific gravity 12·666. (Boussingault.)—*q.* From Otra Mina, near Titiribi. (Boussingault.)—*r.* From the Ural; octohedrons; sp. gr. after fusion, 15·627. The alloys

richer in gold crystallize in dodecahedrons; those which contain less gold, in tetrahedrons and octohedrons. (Awdejew.)—*s.* From Sta. Rosa de Osos; sp. gr. 14·149 [?]. (Boussingault.)—*t.* From Transylvania. (Boussingault.)—*u.* Electrum from Schlangenberg, in Siberia. (Klaproth.)—*v.* From Sivänowski, in the Altai mountains; sp. gr. after fusion, 14·556. (Rose.)—*w.* From Veröspatak, in Transylvania. (Rose.)—*x.* Auriferous Silver from Konigsberg. (Fordyce.)

B. Telluride of Gold and Silver.—*a. Auriferous Telluride of Silver.*—Found in indistinct crystals, which appear to belong to the oblique prismatic system; they have a semi-conchoidal fracture, and vary in density from 8·72 to 8·83. Sometimes slightly malleable, sometimes not at all. Have a stronger lustre and somewhat darker colour than pure telluride of silver. (Petz, *Pogg.* 57, 470.)

| | | | Petz. From Nagyag. |
|---|---|---|---|
| 5Ag | 540 | 48·09 | 46·76 |
| Au | 199 | 17·72 | 18·26 |
| 6Te | 384 | 34·19 | 34·08 |
| 5AgTe,AuTe | 1123 | 100·00 | 100·00 |

*b. Graphic Tellurium.*—Acute rhombohedrons (*Fig.* 151); also obtuse rhombohedrons, with an axis of only half the length of the former, and truncated. (*Fig.* 142.) (Breithaupt, *Schw.* 52, 170.) According to others, the mineral belongs either to the right prismatic or the oblique prismatic system of crystallization, and crystallizes in needles. Sp. gr. 8·28. (Petz.) Soft and sectile. Colour, light steel-grey. When it is heated in an open tube, a grey sublimate of tellurium collects in the part of the tube immediately adjoining, and in the farther part, a white sublimate of tellurous acid, which fuses into transparent drops. Fuses upon charcoal, emitting a slightly acid odour, not resembling that of horse-radish; covers the charcoal with a white deposit; and is reduced to a dark grey metallic globule, which is converted by long blowing into a pale yellow alloy of gold and silver, exhibiting incandescence at the moment of solidification. (Berzelius.) Dissolves in aqua-regia, with separation of chloride of silver, and forms a solution which gives a white precipitate on dilution with water.

| | | | Petz. | | Klaproth. | Berzelius. |
|---|---|---|---|---|---|---|
| *Graphic Tellurium*, from Offenbanya. | | | *a.* | *b.* | | |
| Ag | 104 | 13·85 | 11·47 | 11·31 | 10 | 11·53 |
| Au | 199 | 26·50 | 26·97 | 26·47 | 30 | 24·00 |
| 7Te | 448 | 59·65 | 59·97 | 58·81 | 60 | 51·50 |
| Pb | | | 0·25 | 2·75 | | 1·50 |
| Cu | | | 0·76 | | | |
| Sb | | | 0·58 | 0·66 | | 11·47 |
| Fe; As; S. | | | | | | |
| $AgTe^4$,$AuTe^3$? | 751 | 100·00 | 100·00 | 100·00 | 100 | 100·00 |

The mineral *a* was made up of fine needles; *b* of thick needles. (Petz, *Pogg.* 57, 472.) Part of the silver appears to be replaceable by copper and lead.

*c. White Tellurium.*—Crystalline system the right prismatic? Crystallizes in needles. Sp. gr. 7·99 to 8·33. Soft, brittle. Colour, silver-white, inclining to yellow. Before the blowpipe, it behaves like Foliated Tellurium, excepting that it does not give off sulphurous acid. (Berzelius.) Dissolves in nitric acid, leaving a residue of gold.

| | *White Tellurium.* | | Petz. | | | | | Klaproth. |
|---|---|---|---|---|---|---|---|---|
| | Nagyag. | | *a.* | *b.* | *c.* | *d.* | *e.* | |
| Ag | 104 | 15·14 | 14·68 | 10·69 | 7·47 | 10·40 | 12·78 | 8·50 |
| Au | 199 | 28·97 | 24·98 | 28·98 | 27·10 | 25·31 | 29·62 | 26·75 |
| 6Te | 384 | 55·89 | 55·39 | 48·40 | 51·52 | 44·54 | 49·96 | 44·75 |
| Pb | .... | .... | 2·54 | 3·51 | 8·16 | 11·21 | 13·82 | 19·50 |
| Sb | .... | .... | 2·50 | 8·42 | 5·75 | 8·54 | 3·82 | .... |
| S | .... | .... | .... | .... | .... | .... | .... | 0·50 |
| $AgTe^3,AuTe^3$ | 687 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

*a.* Long white prisms, of sp. gr. 8·27.—*b.* White, thick prisms, sp. gr. 7·99.—*c.* Short, yellowish prisms, with less distinct cleavage; sp. gr. 8·33.—*d.* and *e.* Light yellow, crude masses, exhibiting no cleavage. The silver is partly replaced by lead, and the tellurium by antimony [?]. White Tellurium and Graphic Tellurium are probably the same mineral, their common formula being $AgTe,2AuTe^3$. (Petz, *Pogg.* 57, 473.)—According to the atomic weight of gold, adopted in this Handbook, the preceding formula should be: $AgTe,AuTe^6 = AgTe^4,AuTe^3$; but for this, the proportion of tellurium given by the analyses of White Tellurium is too small; hence the formula $AgTe^3,AuTe^3$ is to be preferred.

C. Alloy of Gold, Silver, and Copper.—The combination of gold with copper and silver together, is attended with a greater amount of expansion than the combination with copper alone. 22 pts. of gold with 1 silver and 1 copper form an alloy whose specific gravity is 17·344. The alloy is hard, and inclines to yellow, red, or white, accordingly as the gold, copper, or silver predominates.

D. Amalgam of Gold and Silver.—A solution of 1 loth ($\frac{1}{2}$ oz.) of gold in 100 pounds of mercury is liquid, and may be completely squeezed through leather. But if 8 loth of silver be likewise dissolved in the liquid, and the product pressed through leather, 56·5 loth of amalgam remain in the leather, containing 1 loth of gold and 7·5 loth of silver. The whole of the gold, together with the greater part of the silver, is therefore separated in the form of a solid amalgam. (Wehrle, *Zeitschr. Phys. Math.* 9, 414.)

## Other Compounds of Gold.

With Platinum, Palladium, Rhodium, Iridium, and Osmium.

## Chapter XXXIX.

# PLATINUM.

*Memoirs relating to Platinum, Palladium, Rhodium, Iridium, and Osmium together.*

Fourcroy & Vauquelin. *Ann. Chim.* 48, 177; also *A. Gehl*, 2, 269.—*Ann. Chim.* 50, 5; also *A. Gehl*, 2, 262.—*Ann. du. Mus. d'hist. nat.* 7, 401; also *Gilb.* 24, 209; also *N. Gehl*, 2, 672.

Vauquelin.—Decomposition of Platinum-ore. *Ann. Chim.* 88, 167; also *Schw.* 12, 265; also *A. Tr.* 24, 1, 273.—*Ann. Chim.* 89, 150; also *Schw.* 24, 21.

Berzelius.—Decomposition of Platinum-ore, and examination of the individual metals composing it. *Pogg.* 13, 435 and 527; 15, 208.

Osann.—Russian Platinum-ore and new metals contained therein. *Pogg.* 8, 505; 11, 311; 13, 283; 14, 329; 15, 158.—*Kastn. Arch.* 10, 100; 16, 129.

Claus.—Ruthenium, a new metal contained in Platinum-ore. *Pogg.* 64, 192; 65, 200; abstr. *Jahresber.* 25, 205; *Ann. Pharm.* 56, 257.—Contributions to the Chemistry of the Platinum-metals. *Ann. Pharm.* 63, 337.

*Memoirs relating exclusively to Platinum.*

Th. Scheffer.—*Abhandl. d. Schwed. Ak. d. Wissensch.* Hamb. & Leipz. 1755. B. 14, s. 275.

Marggraf.—*Chymische Schriften.* Berl. 1761, 1, 1.

Bergman.—*Opusc.* 2, 166.

Fourcroy & Vauquelin.—*Ann. Chim.* 48, 177; 49, 188.

Graf von Sickingen. *Versuche über die Platina.* Mannheim, 1782.

Proust.—*Ann. Chim.* 38, 146 and 225; also *Scher. J.* 7, 256.—*Ann. Chim.* 49, 177; also *N. Gehl*, 1, 347.

Berzelius.—Oxygen and Chlorine-compounds of Platinum. *Schw.* 7, 55; 34, 81.—Platinate of Potash. *Jahresbericht*, 9, 110.

Edmund Davy.—Phosphide and Sulphide of Platinum. *Phil. Mag.*; also *Schw.* 10, 382.—Platinum-salts. *Phil. Mag.* 20, 350.—Fulminating Platinum. *Ann. Phil.* 9, 229; also *Schw.* 19, 91.—Platinum-black, Protoxide of Platinum, and Sulphate of Platinum. *Phil. Trans.* 1820; *Schw.* 31, 340.

Vauquelin.—Sulphide of Platinum. *Ann. Chim. Phys.* 5, 260; also *Schw.* 20, 394; also *N. Tr.* 2, 2, 325.—Chloride of Platinum and Bioxide of Platinum. *Ann. Chim. Phys.* 5, 264; also *Schw.* 20, 398.—Triple salts of Platinum and Sulphate of Platinum. *Ann. Chim. Phys.* 5, 392; also *Schw.* 20, 451.

W. Döbereiner.—Platinum-black. *Schw.* 54, 414; 63, 476.—*J. pr. Chem.* 1, 114; 369.—*Ann. Pharm.* 2, 1; 14, 10; 17, 67.—*Pogg.* 28, 181; 36, 308 and 548.—Spongy Platinum. *J. pr. Chem.* 17, 158; 28, 165.—Chloride of Platinum with Alkalis. *Schw.* 66, 289.—*Pogg.* 28, 180.

—Bioxide of Platinum, with Sulphurous Acid. *J. pr. Chem.* 15, 315.

Fischer.—Chloride of Platinum. *Pogg.* 9, 256; *Schw.* 53, 108.—Platinum sal-ammoniac. *Kastn. Arch.* 14, 150.

Bonsdorff.—Salts of Chloride of Platinum. *Pogg.* 17, 250; 19, 337.—Salts of Bromide of Platinum. *Pogg.* 19, 343.

Gros.—Ammonio-salts of Protoxide of Platinum. *Ann. Pharm.* 27, 241; also *Ann. Chim. Phys.* 69, 204.

Reiset.—Ammonio-salts of Protoxide of Platinum. *Compt. rend.* 10, 870; also *Ann. Pharm.* 36, 111; also *J. pr. Chem.* 20, 50.—*Compt. rend.* 11, 711; 18, 1100; also *N. Ann. Chim. Phys.* 11, 417.

Peyrone.—Ammonio-salts of Protoxide of Platinum. *Ann. Pharm.* 51, 1; 55, 205; 61, 178.

Raewsky.—Ammonio-salts of Protoxide of Platinum. *N. Ann. Chim. Phys.* 22, 278; abstr. *Compt. rend.* 23, 353; 24, 1151; also *Ann. Pharm.* 64, 309; 68, 316.—Gerhardt's Observations thereon. *N. J. Pharm.* 14, 315.

Laurent & Gerhardt.—Action of Ammonia on Chloroplatinate of Ammonium. *Ann. Pharm.* 73, 223; *J. pr. Chem.* 46, 511; *Compt. rend. trar. Chim.* 1849, 113.

Gerhardt.—Researches on the Ammoniacal compounds of Platinum. *Compt. rend. trar. Chim.* 1849, 273; abstr. *Compt. rend.* 31, 241.—*Ann. Pharm.* 76, 307.

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*History.* Crude *Platina* (Spanish diminutive of *Plata,* silver) was discovered in the auriferous sand of the river Pinto: it was first brought to Europe in 1741, under the name of *Platina del Pinto,* and was chiefly examined by Watson, Scheffer, Lewis, Marggraf, Bergman, Sickingen, Mussin-Pouschkin, Fourcroy & Vauquelin, Wollaston, Descotils, Tennant, Berzelius, Edmund Davy, and Döbereiner.

*Sources.* 1. Platinum occurs pure and native, mixed only with palladium, in Brazil. (Wollaston, *Schw.* 1, 364.)—2. In combination with palladium, rhodium, iridium, osmium, ruthenium, iron, copper, and lead, and sometimes with silver,—mixed also with grains of osmium-iridium, gold, titaniferous iron, chrome-iron-ore, hyacinth, spinelle, and quartz, and with gold-amalgam, which remains behind after the extraction of the gold by mercury,—in *Crude Platinum-ore,* or *Crude Platina,* or in *Platiniferous sand.* The latter is found chiefly in rivers and alluvial deposits; seldom in the rock. In the Pinto; in the gold-washings of Barbacoas, in the province of Antioquia; in the province of Choco, in New Granada; and in the provinces of Matto Grosso and Minas Geraes, in Brazil. In veins of manganese in the weathered syenite near Sta. Rosa de Osos, in the Columbian province of Antioquia (Boussingault, *Ann. Chim. Phys.* 32, 204); in the valley of the Jaky, in St. Domingo (Vauquelin, *Schw.* 1, 362); on the western declivity of the Ural, partly in alluvial deposits, partly injected into greenstone and serpentine (*comp.* G. Rose, *Pogg.* 34, 380);—on the Ratoo mountain, in Borneo. The gold-sand in the north of Ava is likewise interspersed with iron-black, magnetic grains, containing about 20 per cent. of platinum and 60 per cent. of iridium. (Prinsep, *Pogg.* 34, 380.) The gold-sand of the Rhine contains $\frac{1}{2400}$ of platinum. (Fr. Döbereiner, *N. Br. Arch.* 25, 57.) The palladium obtained from the gold of the Wilhelm works on the Harz contains

a small quantity of platinum. (Berzelius, *Pogg.* 34, 380.) D'Angy & Villain (*Pogg.* 31, 16) found platinum in the galena of Consolens and Alloué, in the Dept. de la Charente; Berthier and Descotils did not find it in this galena, but they discovered it in the manganese of Alloué, Epénéde, Planveille, and Melle, of the Depts. Charente and Deux Sévres. Vauquelin's statement (*Ann. Chim.* 60, 317) respecting the occurrence of platinum in a silver-ore from Guadalcanal in Spain, appears, from the more recent observations of Berzelius (*Lehrb.* 1826, 2, 168) to be doubtful. ¶ Platinum has also been found in the gold-washings of Mr. Erwin's works, in Rutherford county, N. America. (Shepard, *Sill. Ann. J.* [2], 2, 253.) According to Molnár (*Haidinger's Berichte,* 3, 412) platinum occurs associated with nickeliferous native iron, in the auriferous sand of Ohlápian, in Hungary. Kapetzky & Kapera (*Haid. Ber.* 3, 439) deny the existence of the platinum, and state that the iron contains no nickel. Molnár, however, on repeating his experiments (*Haid. Ber.* 3, 475), extracted 34 grains of small crystals of magnetic iron, which had particles of platinum adhering to them, and from which he prepared the chloroplatinate of ammonium; he likewise repeats his statement regarding the nickel. From the recent investigations of Pettenkofer (*Pogg.* 74, 316) it would appear that platinum is much more widely distributed than has hitherto been supposed; all silver, excepting that which has been subjected to the particular process of purification described by Pettenkofer, appears indeed to contain platinum (*comp.* pp. 202, 203). ¶

*Composition of crude Platinum Ore.*

| | Berzelius. | | | | Svanberg. | | |
|---|---|---|---|---|---|---|---|
| | *a*,*α*. | *b*,*β*. | *b*. | *c*. | *d*. | *e*. | *f*. |
| Platinum | 78·94 | 73·58 | 86·50 | 84·30 | 86·16 | 84·34 | 55·44 |
| Palladium | 0·28 | 0·30 | 1·10 | 1·06 | 0·35 | 1·66 | 0·49 |
| Rhodium | 0·86 | 1·15 | 1·15 | 3·46 | 2·16 | 3·13 | 6·86 |
| Iridium | 4·97 | 2·35 | | 1·46 | 1·09 | 2·58 | 27·79 |
| Osmium | | | | 1·03 | 0·97 | 0·19 | trace |
| Iron | 11·04 | 12·98 | 8·32 | 5·31 | 8·03 | 7·52 | 4·14 |
| Copper | 0·70 | 5·20 | 0·45 | 0·74 | 0·40 | trace | 8·30 |
| Manganese | | | | | 0·10 | 0·31 | |
| Osmium-iridium | 1·96 | 2·30 | 1·40 | | 1·91 | 1·56 | |
| Grains of sand | | | | 0·60 | | | |
| Lime | | | | 0·12 | | | |
| | 98·75 | 97·86 | 98·92 | 98·08 | 101·17 | 101·29 | |

*a*. From Nischne Tagilsk, in the Ural, distinguished by a very dark grey colour: *α* are the non-magnetic grains, *β*. the magnetic grains, some of them possessing very strong polarity.—*b*. From Goroblogadat, in the Ural, perfectly non-magnetic.—*c*. From Barbacoas, consisting of very large grains. The osmium-iridium in these three ores is in the form of grains and spangles. The spangles are partly fused into the true grains of the platinum ore, and are left behind when it is dissolved in boiling aqua-regia; part of the osmium and iridium is, however, chemically combined with the platinum, and this portion is attacked when the platinum is dissolved. The loss partly arises from volatilization of osmium. (Berzelius.)—*d*. From Choco, freed from iron-ore by the magnet.—*e*. From the Pinto. After separation of the iron-ore, there remained a mixture of grains of various kinds; *α*. Rounded grains, having considerable lustre, and a colour inclining to lead-grey; sp. gr. 17·88: the analysis of these is given under *e*. (*β*. Angular grains, of a light grey colour, and little lustre; sp. gr. 17·08; *γ*. Rough grains, somewhat yellowish, but with

black points; sp. gr. 14·24; δ. Black, shining grains, of sp. gr. 7·99.—*f*. The so-called osmium-iridium, from South America; sp. gr. 16·94. (Svanberg, *Pogg.* 36, 46.)

[Analyses of Siberian platinum-ores by Osann. (*Pogg.* 8, 505; 13, 283; 14, 329; *Kastn. Arch.* 16, 129.)]

According to Vauquelin, the American platinum-ore also contains lead, a statement which Gmelin has confirmed. Wöhler likewise observed silver in the American platinum-ore, and grains of auriferous silver in that from Siberia. Schneider found a native amalgam of gold in the platinum-ore from Columbia (p. 247).

### *Analysis of Platinum-ore, and Preparation of Platinum, Palladium, Rhodium, Osmium, and Iridium.*

#### A. *According to Vauquelin, Wollaston, and others.*

1. The platinum-ore freed by the magnet from the greater part of the iron-ore, is treated with cold, dilute aqua-regia, which extracts gold, mercury, and a certain quantity of iron. When American platinum ore is digested on the water-bath for several days with strong hydrochloric acid, renewed from time to time, as long as the liquid acquires a brown colour, a solution is formed containing a very large quantity of iron, a considerable quantity of manganese, a small quantity of lead, copper, mercury, and platinum,—and on levigating the ore with water, a white powder is obtained, consisting of titanic acid containing chromium. The ore thus treated, leaves, on subsequent digestion with aqua-regia, only 2·6 per cent. of insoluble residue, consisting of shining scales and a small quantity of black powder, whereas, if the previous treatment were omitted, 4·2 per cent. of residue would be left (Gm.).

2. The platina is then dried, and, according to Vauquelin, mixed in a retort with four times its weight of aqua-regia, containing $\frac{2}{3}$ hydrochloric acid of 22° Bm. to $\frac{1}{3}$ fuming nitric acid of 44° Bm. The liquid is gently warmed after a while, then more strongly to drive off the excess of acid, the heat being continued till the solution is so far concentrated as to solidify on cooling. (It is better, however, to follow Berzelius's plan of covering the platiniferous sand only with hydrochloric acid, and adding the nitric acid from time to time; otherwise a large quantity of chlorine will be lost.) The residue is treated with water to dissolve out the soluble portion. (When this residue is treated with water, an evolution of chlorine often takes place, because the bichloride of palladium produced by the action of the acid is thereby partially decomposed: *Berzelius.*) The portion which remains undissolved is repeatedly treated in the same manner with corresponding quantities of aqua-regia, till the liquid no longer acquires a brown colour, whereupon a black powder (*OJ*) amounting to $\frac{1}{27}$ of the whole, remains undissolved. The acid liquid (*Dist.*) which passes over in these distillations, contains, according to Laugier (*Ann. Chim.* 89, 191) a small quantity of osmic acid.

3. The hydrochloric acid solution containing platinum, palladium, rhodium, and a small quantity of iridium, also iron, copper, mercury, and lead (it must be as free as possible from excess of acid) is either treated according to Wollaston's more recent method, by neutralizing any excess of acid that may be present, and adding cyanide of mercury, whereby the palladium is precipitated in yellowish-white flakes of cyanide of palladium (often not appearing till after some time), which when washed and ignited yield *Palladium;*

4. Or, according to Wollaston's older method, and according to Vauquelin's method, the hydrochloric acid solution, without previous precipitation of the palladium, but merely diluted with water in the proportion of 10 parts of water to 1 part of the concentrated solution, is mixed with a solution of sal-ammoniac, whereby the greater part of the platinum is thrown down in the form of platinum-sal-ammoniac. Berzelius recommends the previous addition of a little nitric acid, to prevent the admixture of iridium with the precipitate. Cloud (*Schw.* 43, 316 ; also *Gilb.* 72, 253) employs a solution of sal-ammoniac saturated at a boiling heat, and separates the precipitate quickly from the liquid, before the latter has time to deposit any salts of rhodium or palladium.

5. The yellow precipitate well washed with cold water, and then ignited, yields *Platinum.* Cloud purifies the product by repeated solution in aqua-regia, precipitation by sal-ammoniac, and ignition of the precipitate.

6. From the liquid separated from the yellow precipitate (according to Wollaston, a small quantity of gold may be separated therefrom by neutralizing with carbonate of soda and adding green vitriol), the whole of the noble metals are separated in the form of a black powder (*Red*) by immersing in it a plate of iron (Vauquelin) or of zinc (Wollaston).

7. Cloud cupels the black powder thus obtained (*Red*) with four times its weight of silver, and a quantity of lead sufficient for the separation of the base metals; rolls the resulting alloy, consisting of silver, palladium, platinum, rhodium, a small quantity of gold [and iridium ?] into thin plates ; treats these plates repeatedly with boiling nitric acid; throws down the silver from the solution by hydrochloric acid, and then, after filtering, precipitates the palladium by caustic potash or cyanide of mercury ; digests the undissolved portion, consisting of platinum, rhodium, gold [and iridium ?] in aqua-regia, whereupon the *Rhodium* [and iridium ?] is left behind ; and precipitates *Platinum* from the solution by sal-ammoniac, and *Gold* by green vitriol.

8. Vauquelin and Wollaston wash the black powder (*Red*) with cold water, and afterwards boil it with water to dissolve out the platinum-sal-ammoniac, which has been precipitated together with the black powder in consequence of abstraction of acid. They then treat the precipitate with cold nitric acid, thereby dissolving out iron, copper, lead, and a small quantity of palladium, and afterwards with cold hydrochloric acid, which, besides iron and copper, likewise takes up a small quantity of palladium, platinum, and rhodium, these metals, according to Wollaston's opinion, having been partly precipitated, not in the metallic state, but as oxides. The powder, after another washing with water, is next heated, whereupon, according to Vauquelin, chloride of copper, calomel, metallic mercury, and a black substance resembling osmium, are separated.

9. According to Wollaston's older process for preparing palladium, the powder (*Red*) purified in the manner just described, is treated with a mixture of hydrochloric acid and nitre, which leaves undissolved the chloride of platinum and potassium produced by its own action, and yields a solution chiefly consisting of palladium and rhodium. This solution, when evaporated, deposits crystals of chloride of palladium and potassium, which may be distinguished by their two colours, and mechanically separated from the other crystals, after which the oxide of palladium is mechanically separated by potash, then washed, and converted by ignition into metallic *Palladium.*

10. If the palladium has been separated by (7), the remaining crystal-

lized and uncrystallized mass may be ignited with water, and dissolved in aqua-regia. When the palladium has been separated by (3), the powder (*Red*) is likewise dissolved in aqua-regia. To separate the rhodium from such a solution, Wollaston then adds common salt, and obtains by evaporation chlororhodiate of sodium, a small quantity of chloroplatinate and chloropalladite of sodium, together with protochloride of copper and sesquichloride of iron. The last four salts are removed by triturating and agitating the mass with alcohol of 84 per cent., while the chlororhodiate of sodium remains behind. From the solution of this salt in water, the *Rhodium* is precipitated, by the immersion of a bar of zinc, in black metallic flakes, which turn white on ignition; or the salt is strongly ignited, and the chloride of sodium extracted by water.

11. Vauquelin, on the other hand, to obtain the palladium and rhodium, dissolves the powder (*Red*) purified by (8), in the mixture of hydrochloric and nitric acid mentioned in (2), whereupon a small quantity of iridium is left behind in the form of a black powder, provided the treatment with this acid is not too often repeated.

12. The hydrochloric acid solution (11) of platinum, palladium, rhodium, and a certain quantity of iridium, also containing copper and iron, is next freed from excess of acid by evaporation to a syrupy consistence, diluted with 10 parts of water, and the greater part of the remaining platinum precipitated by sal-ammoniac in the form of a yellow double salt, which, when washed and ignited as above (5), yields *Platinum.*

13. The liquid separated from the chloroplatinate of ammonium, together with the wash-water, is evaporated nearly to dryness, the mass again dissolved in cold water, which leaves behind an orange-yellow or aurora-red compound of chloroplatinate of ammonium with a small quantity of chloriridiate of ammonium; and this, by ignition and subsequent treatment with aqua-regia, may be separated into a solution of platinum and an insoluble residue of *Iridium.*

14. Vauquelin then dilutes the cold aqueous solution of (13) with a proper quantity of water; perhaps mixes it with a small additional quantity of sal-ammoniac; and adds ammonia in small portions and with constant agitation, so long as fine rose-coloured scales of ammonio-chloride of palladium continue to fall down. These are washed, first with cold and then with hot water—and likewise with water slightly acidulated with hydrochloric acid, if any ferric oxide or oxide of rhodium has been thrown down by the addition of too much ammonia—and then converted into *Palladium* by ignition.

15. Vauquelin next evaporates the liquid separated from the palladium-salt, sufficiently to make it solidify in a crystalline mass on cooling. Chloropalladite of ammonium then crystallizes in yellowish-green four-sided prisms, and chlororhodiate of ammonium in ruby-coloured, six-sided prisms. The remaining mother-liquid, mainly consisting of solution of protochloride of copper and sesquichloride of iron, is poured off; the crystals pulverized in a porcelain mortar; set aside in a vessel with alcohol of 36° Bm.; and the liquid frequently agitated. After 24 hours, the alcohol is poured off and replaced by a fresh portion, the process being repeated as long as the liquid acquires a yellowish-green tint.

16. As the chlororhodiate of ammonium which remains after washing with alcohol may still contain a little chloroplatinate of ammonium, Vauquelin dissolves it either in pure water or in water slightly acidu-

lated with hydrochloric acid, which leaves the platinum-salt behind. The solution evaporated to dryness and ignited, yields *Rhodium*.

17. The noble metals dissolved by the hydrochloric and nitric acid, which were used to purify the black powder (*Red*), having been precipitated by iron from these acids, the precipitate may be resolved into platinum, palladium, and iridium, by a process similar to that described for the treatment of the powder (*Red*), (11 to 18). (Vauquelin.)

18. The black powder (*O J*) (2), which, according to Vauquelin, mainly consists of iridium and osmium, but likewise contains chrome-iron ore, titaniferous iron, quartz-sand, spinelle, and hyacinth, may be separated by elutriation into a fine and comparatively pure powder, having somewhat of the aspect of black lead, and coarser grains containing a larger proportion of chrome-iron ore. (Vauquelin.) The powder (*O J*) is mixed, according to Vauquelin, with twice its weight of nitre, and heated in a porcelain retort to which is adapted a tube dipping into lime-water, as long as gas continues to go off. At first yellow flakes of osmiate of lime are formed in the lime-water; but they are afterwards dissolved by the nitrous acid which passes over; needles of osmic acid likewise collect in the glass tube at the beginning of the action, but afterwards pass over into the lime-water.

19. The mass which remains in the retort yields, by repeated boiling with water, a red-brown solution no longer smelling of osmium; but containing iridic, osmic, titanic, and ferric oxides, alumina, and a small quantity of chromic oxide in combination with potash. (Vauquelin.)

20. The washed powder is treated with concentrated hydrochloric acid, which thereupon acquires a dark green colour, chiefly by taking up iron and iridium. (Vauquelin.)

21. The powder which remains after the treatment with hydrochloric acid, is again fused, as above described, with 2 parts of nitre, then once more treated with water, and subsequently with hydrochloric acid,—and this treatment with nitre, water, and hydrochloric acid is repeated till the whole of the powder is dissolved, partly in water, partly in hydrochloric acid. The solution of the final residue is further accelerated by the use of aqua-regia. In these latter processes, the hydrochloric acid acquires more of a blue than of a green colour, inasmuch as the quantity of iron present is not so great as before. (Vauquelin.)

(Wollaston, instead of igniting the powder (*O J*) with nitre in a retort, mixes it with 1 to $1\frac{1}{2}$ pt. hydrate of potash, and ignites it for an hour in a silver crucible, after which he likewise treats it first with water, then with hydrochloric acid, then again with hydrate of potash, &c.)

22. Vauquelin neutralizes the alkaline liquids obtained in (19) and in the subsequent treatment with water, by the addition of nitric acid, whereby green flakes are precipitated, consisting of iridic, osmic, titanic, and chromic oxides, alumina, and silica. The supernatant liquid contains nitrate and chromate of potash, and osmic acid, which may be separated in the aqueous form by distillation.

23. The green flakes are dissolved in hydrochloric acid, the solution mixed with the hydrochloric acid liquid of (20) and with the other solutions subsequently obtained in the same manner; nitric acid is then added to bring the iridium to its highest state of oxidation, and thereby prevent it falling to the bottom when heated, in combination with ferric oxide, titanic oxide, and silica; after which, the osmic acid is distilled off by long-continued boiling, and collected in a cooled receiver. (Vauquelin.)

24. Vauquelin dilutes the residual liquid in the retort with water, and precipitates the titanic oxide and part of the ferric oxide by nearly neutralizing it with ammonia; he then filters the solution, evaporates again, and by the addition of sal-ammoniac, precipitates the chloriridiate of ammonium in small, black crystals, which, when ignited and freed by washing from adhering chloride of potassium, yield *Iridium*.

25. The remaining liquid, after dilution with water, is supersaturated with ammonia, which precipitates the ferric oxide, and retains the iridic oxide in solution; and the *Iridium* therein contained is separated by filtering and evaporating the liquid, igniting the residue, and washing out the adhering chloride of potassium.

26. The liquid (*Dest.*), of (2) containing hydrochloric, nitric, and osmic acid is, according to Laugier (*Ann. Chim.* 89, 191; also *Schw.* 19, 70), nearly neutralized with milk of lime and distilled to dryness. The distillate containing osmic acid is then mixed with the lime-water of (16) containing the same compound, and with the distilled liquids of (22) and (23) also containing osmic acid. This mixture, if it does not already contain sufficient acid, is mixed with a moderate excess of hydrochloric acid, and decomposed by zinc. (If too much hydrochloric acid is added, the blue cloud is redissolved, and a purple solution formed; if too little, part of the osmium remains in solution, so that the liquid still retains the odour of osmic acid, and, the formation of gas-bubbles being but slow, the precipitated osmium is deposited upon the zinc: *Vauquelin.*) The black flakes of *Osmium* which fall to the bottom, are several times washed—after the chloride of zinc has been decanted—first with water containing sulphuric acid, and then with pure water, after which they are dried at a gentle heat, and preserved in stoppered bottles. (Vauquelin.)—A considerable quantity of osmic acid escapes with the hydrogen gas. (Berzelius.)

### B. *According to Berzelius.*

#### *a. Complete process, adapted for Quantitative Analysis.* (*Pogg.* 13, 553.)

1. The ore, after being freed from grains of foreign matter by mechanical separation and by the magnet, is treated with dilute hydrochloric acid, which dissolves ferric oxide and metallic iron.

2. It is then heated in a tubulated retort, having a cooled receiver adapted to it, with concentrated hydrochloric acid, to which strong nitric acid is added from time to time, as the action diminishes in intensity. An excess of nitric acid must be avoided, because it would decompose the chloride of iridium, and cause the separation of oxide of iridium on evaporation. The heat is continued till the residue in the retort becomes syrupy and solidifies on cooling, the saline mass dissolved in a small quantity of hot water, and the solution carefully decanted from the insoluble residue. The distillate, which has a yellowish colour, arising from chloride of platinum, which has spirted over, is then poured upon the residue, and distilled again, without boiling, whereupon a colourless distillate of dilute osmic acid is obtained. Should the residue still contain any soluble matter, it must be again treated in the same manner with aqua-regia.

3. The distillate is neutralized with ammonia or lime; saturated with hydrosulphuric acid gas in a bottle nearly filled with it; and set aside for some days with the bottle closed, till the precipitate settles down; after

which the watery liquid is separated from the sulphide of osmium by decantation and filtering.

4. The metallic solution, together with the undissolved portion (2), often smells of chlorine, arising from decomposition of bichloride of palladium; in that case, it must be boiled till the bichloride is converted into protochloride, and the odour is entirely destroyed; if a turbidity should be produced during the ebullition, from separation of oxide of palladium, that substance must be dissolved [in hydrochloric acid?]. The solution is then separated by filtration from the undissolved portion.

5. The filtrate (4) is mixed with twice its volume of alcohol of sp. gr. 0·833, and then with a saturated aqueous solution of chloride of potassium, as long as a precipitate is formed.

6. The precipitate, consisting of chloroplatinate and chloriridiate of potassium, together with a small quantity of chlororhodiate and chloropalladiate of potassium, is washed with alcohol of 60 per cent., containing a small quantity of saturated aqueous solution of chloride of potassium, till the filtrate no longer gives a precipitate with sulphuretted hydrogen.

7. The precipitate (6), immediately after drying, is intimately mixed with dry carbonate of soda, and very gently heated in a porcelain crucible—together with the ashes of the filter, and the excess of carbonate of soda—till the mass is blackened to the very centre and begins to fuse. The platinum is then left in the metallic state, and the iridium and rhodium in the state of oxides, but not soluble in acids. (If the solution had been precipitated with sal-ammoniac instead of chloride of potassium, the last two metals would likewise have been left in the metallic state, and would have dissolved in the aqua-regia together with the platinum.) The black mass is freed by water from the greater part of the potash and soda-salt, and the alkali which adheres to the oxides of rhodium and iridium is dissolved out by dilute hydrochloric acid. In this process, the hydrochloric acid always dissolves a certain quantity of platinum and iridium, inasmuch as the oxide of iridium supplies the oxygen necessary for that purpose. (Hermann, *Pogg.* 37, 408.) The residue is washed on a filter, dried, ignited, and weighed: the filter, however, must be ignited alone, in order that it may not exert any reducing action.

8. The ignited mass is fused with six times its weight of bisulphate of potash; the fused product dissolved in water, and the undissolved portion repeatedly treated in the same manner with bisulphate of potash and water, as long as it imparts any colour to the liquid.

9. The resulting solution, which contains the oxide of rhodium, is mixed with excess of carbonate of soda, evaporated to dryness, and ignited in a platinum crucible. The mass is then dissolved in water, the oxide of rhodium washed on a filter, ignited in contact with the filter, and reduced in a stream of hydrogen gas. The *Rhodium* thus obtained often contains a small quantity of palladium, which may be dissolved out by aqua-regia, and precipitated from the solution, after neutralization, with cyanide of mercury.

10. The remaining mixture of platinum and oxide of iridium (8), is digested with very dilute aqua-regia, which extracts the greater part of the platinum, after which the solution is decanted.

11. To purify the oxide of iridium from the remaining portion of platinum, it is mixed with strong aqua-regia, containing a little common salt (whereby the conversion of bichloride of platinum into protochloride on evaporation is prevented), and the liquid evaporated to dryness; the

mass is then digested in water, and the oxide of iridium washed on the filter, first with a weak solution of common salt, and afterwards with a weak solution of sal-ammoniac, because, if washed with pure water, it would run through the filter.

12. The solution which passes through the filter contains a small quantity of oxide of iridium, together with the platinum; it is therefore mixed with carbonate of soda, and evaporated to dryness; the residue ignited; the saline matters dissolved out from it by water, and the platinum by aqua-regia, the greater part of the oxide of iridium remaining undissolved. The very small portion of oxide of iridium which dissolves, together with the platinum, is precipitated, on the addition of ammonia, in brown flakes containing a very small quantity of platinum.

13. The oxide of iridium obtained by (11) and (12) is freed from sal-ammoniac by ignition, and reduced by hydrogen.

14. The alcoholic filtrate (6) containing palladium, rhodium, iron, and copper, together with small quantities of platinum, iridium, and manganese, is put into a bottle, and saturated with hydrosulphuric acid gas; it is then closed with a ground stopper, set aside for 12 hours in a warm place, to promote the precipitation of the metallic sulphides, and filtered. The filtrate, which is often coloured red from the presence of sesquioxide of rhodium or iridium, is evaporated; the metallic sulphide which then falls down is added to the portion previously precipitated; the liquid poured off from that portion of sulphide which has settled upon the sides of the vessel, in the form of an unctuous fetid mass; the latter washed with water, and dissolved in aqueous ammonia, and the solution evaporated in a platinum crucible.

15. The remaining, and still moist portion of the metallic sulphides (palladium, rhodium, iridium, and copper), is also put into the same crucible, and roasted as long as sulphurous acid continues to go off, after which the mass is digested in strong hydrochloric acid.

16. The hydrochloric acid solution of (15), containing palladium and copper, leaves, when evaporated with chloride of potassium and nitric acid, a dark saline mass, from which alcohol of sp. gr. 0·833 dissolves the free chloride of potassium, and likewise chloride of copper and potassium, together with a mere trace of palladium (to be precipitated with cyanide of mercury), while the greater part of the chloride of palladium and potassium remains undissolved. The residue, after being washed on the filter with alcohol, is dissolved in water, and the solution treated with cyanide of mercury; the resulting precipitate of cyanide of palladium yields, when ignited, metallic *Palladium*.

17. The metallic sulphides (15), after roasting and exhaustion with hydrochloric acid, are fused with bisulphate of potash, exhausted with water, again fused with bisulphate of potash, &c., till the water no longer becomes coloured by taking up oxide of rhodium. This solution, which contains the greater part of the oxide of rhodium, often mixed with a little protoxide of palladium, is treated as in (9).

18. The mass exhausted by bisulphate of potash is resolved, by digestion in aqua-regia, into a small quantity of *Platinum*, which dissolves, and *Iridium*, which remains behind.

19. The liquid, from which the metallic sulphides (14) have been precipitated, contains iron, together with small quantities of iridium and rhodium, and a trace of manganese; it is treated with nitric acid, to bring the iron completely into the state of sesquioxide, and then precipitated by ammonia.

20. The precipitate contains ferric oxide, together with the oxides of iridium and rhodium, and a small quantity of silica (which remains behind when the oxides are dissolved in hydrochloric acid). It is reduced by hydrogen gas, and freed from iron by hydrochloric acid, which is heated towards the end of the operation. Iridium and rhodium then remain in the form of a peculiar black powder, which, when gently heated in the air, decrepitates with incandescence, but in close vessels gives out water without incandescence.

21. The liquid (19), after precipitation by ammonia, is evaporated with a quantity of carbonate of soda sufficient to decompose the ammoniacal salts; the residue gently ignited, exhausted with water (if too much heat has been applied, the water acquires a yellow colour from dissolved oxides), then with hydrochloric acid, which takes up the manganese; and the remaining mixture of oxides of rhodium and iridium is added to the metallic sulphides (15) which have been roasted and treated with hydrochloric acid; so that the whole may be fused, as described in (17), with bisulphate of potash.

23. The portion of the platinum ore (4) which is insoluble in aqua-regia consists of grains and scales of the alloy of osmium and iridium, of sp. gr. 15·78; of grains of sand, and other foreign bodies; and likewise, if too much nitric acid (2) has been used in dissolving the platinum ore, of oxide of iridium, in the form of a black powder, which looks like charcoal, and has a great inclination to run through the filter. It is broken up in a steel mortar, or on the anvil, with a steel hammer; then pulverized as finely as possible in a stone-ware mortar; the powder freed by long boiling with hydrochloric acid from the iron which has been introduced into it from the mortar, and mixed, after drying, with an equal weight of nitre (if a larger quantity of nitre is used, or if combustible matters are present, the mass is very apt to froth over). The mixture is then heated in a porcelain retort, gently at first, and afterwards to a full red heat, as long as gas continues to escape; and the vapours of osmic acid are passed into a tubulated receiver, and thence through a connecting tube into a bottle containing dilute ammonia. (Instead of the nitre, Fischer recommends nitrate of lime, which, he says, decomposes the osmium-iridium more easily; so that a capacious glass retort may be used in place of the porcelain retort.)

24. The mass is mixed with water, to dissolve all the saline constituents; the mixture put into a tubulated retort; the solution, when clear, decanted off; water again poured on the residue in the retort; and the liquid again decanted.

25. The decanted liquids which contain potash in combination with nitric, silicic, chromic, and osmic acid, together with a little sesquioxide of iridium, are distilled with hydrochloric acid (but without actual boiling, otherwise portions will spirt over), whereupon all the osmic acid passes over. [The iridium left in the residue is probably obtained by the method described in (27)?]

26. The substance which remains undissolved in the retort is distilled with hydrochloric acid in the water-bath, till a sample taken out of the retort no longer exhibits any traces of osmic acid. The distillate contains osmic acid, together with a small quantity of chlorine.

27. *a*. The residue in the retort is treated with a small quantity of water, which dissolves hydrochlorate of chromic oxide, and is then thrown upon a filter; the chloriridiate of potassium which there remains is freed

from adhering hydrochlorate of chromic oxide by washing with alcohol. (The aqueous and alcoholic solution, when diluted with water, deposits titanic oxide, mixed with silica and zirconia.) The chloriridiate of potassium is ignited with carbonate of soda in a porcelain retort, in order to collect any osmic acid that may be volatilized. The residue is treated with water, and the undissolved oxide of iridium freed from any platinum that might be mixed with it by boiling with aqua-regia, and from rhodium by fusion with bisulphate of potash. The oxide of iridium, which obstinately retains a small quantity of osmium, is reduced at a very gentle heat by a stream of hydrogen, afterwards kept at a red heat in the air, as long as osmium continues to oxidize and go off in vapour; again reduced by hydrogen and once more oxidized in the air; and the greater part of the osmium thereby removed. If, however, too strong a heat be applied, the two metals combine intimately and shrink together, whereby the combustion of the osmium is rendered more difficult. The reduced iridium may also be gently ignited in a stream of oxygen or chlorine gas, and the gas passed into ammonia, to prevent any of the osmium from escaping.

*β*. Or, instead of 26 and 27: The portion insoluble in water, instead of being treated with hydrochloric acid, is distilled in the water-bath with excess of nitric acid, till a portion taken out of the retort no longer gives out any odour of osmium. [This process likewise does not separate all the osmium, but much more than the former; moreover, the distillate is free from chlorine and nitric acid.] The dark purple nitric acid solution leaves, on evaporation, a residue of nitre and nitrate of protoxide of iridium. The residue, insoluble in nitric acid, is washed and treated with nitric acid, which forms a green mass, and, if the heat be continued, dissolves nearly the whole as *Sesquichloride of Iridium*, forming a green solution, and causing an evolution of chlorine. If strong aqua-regia be used instead of hydrochloric acid, a solution of *Bichloride of Iridium* is obtained.

28. During the distillation (25 or 26), part of the osmic acid sublimes in the crystalline form, and the rest dissolves in the water which passes over. The first fourth of the distillate contains the largest quantity of osmic acid; the last three-fourths contain but little of it, and may be contaminated with chloride of iridium mechanically carried over. For the preparation of metallic osmium from the aqueous solution, the two following methods are used:

*α*. The solution is mixed with a small quantity of hydrochloric acid, and digested with mercury at 40° in a closed flask. The liquid gradually acquires a brownish colour, from formation of protochloride of osmium, but becomes colourless after several days' digestion, the chloride of osmium being decomposed, and a mixture formed, consisting of calomel, pulverulent osmium-amalgam, and excess of mercury containing a portion of the amalgam in solution. This mixture, when washed and dried, then placed in a retort or a widened glass tube, and heated in a stream of hydrogen gas, leaves osmium in the form of a black powder or a porous mass. If the liquid above the mixture is still somewhat coloured, and therefore contains osmium, it is mixed with ammonia, evaporated to dryness, and the residue ignited in a retort; the osmium reduced by the hydrogen of the ammonia remains behind.

Or, *β*. The osmic acid is supersaturated with ammonia; the light yellow mixture heated for several hours to a temperature between 40° and 60° in a flask not perfectly closed, whereupon it gives off nitric oxide, becomes darker, and ultimately black-brown and opaque; the liquid then

left in a basin to evaporate, which gives rise to evolution of ammonia and precipitation of a compound of ammonia with sesquioxide of osmium; and the precipitate washed upon a filter. Should the filtrate be still coloured brown or yellow by sesquioxide of osmium, which happens when the liquid contains hydrochloric or nitric acid, the oxide must be precipitated by evaporation with caustic potash. The compound of ammonia and sesquioxide of osmium obtained by both these methods is dissolved in warm concentrated hydrochloric acid; the solution evaporated to dryness after the addition of a small quantity of sal-ammoniac; and the residue heated in a retort, as long as hydrochloric acid, nitrogen, and sal-ammoniac continue to escape. The osmium is then left in the form of a lead-grey mass, having the metallic lustre.

*b. Shorter Process, adapted to the Preparation of the five Metals.* (*Lehrbuch.*)

1—4. As in *a*.

5. The filtrate (4) is precipitated by excess of a saturated aqueous solution of chloride of potassium, without previous addition of alcohol.

6. The precipitate is washed with the saturated solution of chloride of potassium, till the liquid which runs through is no longer coloured blue by ferrocyanide of potassium.

7. *Platinum and Iridium.* The precipitate is then dried, intimately mixed with twice its weight of carbonate of potash, and gradually heated till the mass begins to melt. This mass is treated with water, and afterwards with dilute hydrochloric acid, and the mixture of platinum and oxide of iridium is collected on a filter, washed with water, and dried.—8 and 9 are thus dispensed with.

10—12. From the mixture on the filter, the greater part of the platinum is extracted in the pure state by dilute aqua-regia slightly heated, and afterwards the rest of the platinum by strong aqua-regia, with addition of common salt, as in *a*, 11. But as the latter solution also contains iridium, it is precipitated with chloride of potassium—the precipitate treated, as in *a*, 7, with carbonate of potash, water, hydrochloric acid, and water—and the pure platinum extracted from the residue by aqua-regia. The pure platinum solutions thus obtained, which should exhibit an orange-yellow colour (not a brown, as that would indicate the presence of iridium), are precipitated by solution of sal-ammoniac, and the precipitate of chloroplatinate of ammonium gradually heated to low redness (if the heat be too rapidly applied, the chloride of platinum partly volatilizes with the sal-ammoniac). The residue is pure *Platinum*. The liquid, after precipitation by sal-ammoniac, still contains a certain quantity of platinum; on dissolving sal-ammoniac in it, the greater part of the platinum is precipitated as chloroplatinate of ammonium; and the whole of that metal is obtained by evaporating the liquid to dryness, and igniting the residue.

13. The oxide of iridium (10 to 12) is reduced by hydrogen to the state of metallic *Iridium*.

14—16. *Palladium.* The liquid (5) from which the chloroplatinate and chloriridiate of potassium have been precipitated by chloride of potassium, together with the wash-water (6), contains palladium, rhodium, copper, and iron, still mixed with a small quantity of platinum and iridium. It is acidulated with hydrochloric acid, and the noble metals, together with the copper, precipitated by a plate of zinc or iron. The precipitate is digested with hydrochloric acid, well washed with water,

and dissolved in aqua-regia: the solution neutralized as exactly as possible with carbonate of soda, and precipitated by cyanide of mercury. The precipitated cyanide of palladium, which is coloured somewhat greenish by copper, is then washed with water, and ignited; the residual palladium, containing copper, dissolved in aqua-regia; a quantity of chloride of potassium added, equal to half the weight of the palladium; the solution evaporated to dryness, finally with addition of a small quantity of aqua-regia; and the residual dark-red chloropalladite of potassium pounded up, washed with alcohol, which extracts the chlorocuprate of potassium, and then ignited in a porcelain crucible, either strongly by itself, or more gently with addition of sal-ammoniac. The residue consists of *Palladium.*

17—20. *Rhodium.* The liquid, after precipitation by cyanide of mercury, together with the wash-water (14—16), containing rhodium and copper, together with small quantities of platinum and iridium, and likewise mercury, is mixed with hydrochloric acid and evaporated to dryness, to drive off hydrocyanic acid.—*a.* The residue, after being dried and finely pulverized, is either digested in alcohol of sp. gr. 0·837, which dissolves the chloroplatinate, chlorocuprate, and chloromercurate of sodium [also the chloriridiate], and leaves the chlororhodiate in the form of a dark-red powder; and this, after sufficient washing with alcohol, is ignited either strongly by itself, or gently in a current of hydrogen gas, after which the *Rhodium*, which remains in the form of a white, coherent mass, is purified from chloride of sodium by water.—Or, *β.* The dry residue is mixed with $1\frac{1}{2}$ times its weight of carbonate of potash, and ignited; the potash-salts dissolved out by water, and the cupric oxide by hydrochloric acid; the residue mixed with 5 times its weight of bisulphate of potash; the mass kept in a state of red-hot fusion in a covered crucible, till it shows an inclination to solidify; the fused product boiled with water; and the undissolved portion repeatedly treated with bisulphate of potash and water, till the potash-salt no longer becomes coloured when fused. The rhodium solutions thus obtained, when evaporated and ignited with excess of carbonate of potash, leave a residue, which, after washing with water, yields oxide of rhodium; and this, when ignited either strongly *per se*, or gently in contact with hydrogen, leaves metallic *Rhodium.*

23—26. *Iridium* and *Osmium.* As in *a*, 23—26.

27. *Iridium.* The residue (25) which remains after distillation with hydrochloric acid [and likewise that of 24?], is diluted with water sufficiently to enable the liquid to pass through the filter. The substance which remains on the filter is washed with alcohol of 60 per cent., as long as the liquid which runs through exhibits a green colour.—*a.* The filtrate, together with the alcohol used in washing (containing titanium, chromium, iron, and a little iridium), is evaporated to drive off the alcohol, then diluted with water and boiled—whereby titanic acid is precipitated—after which it is filtered, and the iridium precipitated from the filtrate by zinc.—*b.* The mass washed with alcohol gives up the chloriridiate of potassium to boiling water. The filtrate is evaporated to dryness; the residue intimately mixed with twice its weight of carbonate of potash, and heated in a silver crucible, till it begins to fuse (in a platinum crucible, chloriridiate of platinum might be formed before the potash had begun to exert its decomposing action); the chloride of potassium and carbonate of potash dissolved out by water; the sesquioxide of iridium—which is still contaminated with osmium, rhodium, platinum, and perhaps with palladium—washed on the filter with water containing sal-ammoniac (if pure

water were used, the sesquioxide of iridium would run through the filter), then freed from platinum by digestion in aqua-regia, and from rhodium and palladium by repeated fusion with bisulphate of potash and subsequent digestion in water; and lastly, the oxide of iridium is washed with boiling water, and the iridium reduced from it, either by strong ignition *per se*, or by moderate ignition in an atmosphere of hydrogen.

With the purer grains of osmium-iridium, which are white and strongly lustrous, have a specific gravity of 18·644, and are much richer in osmium, and not contaminated with foreign metals, the best mode of proceeding is to ignite the mass with nitre—heat the product over the water-bath with excess of nitric acid, whereby the osmic acid is distilled over—dilute the residue in the retort with water—filter—and evaporate the pale purple filtrate containing nitre and nitrate of iridic oxide, till the excess of nitric acid is driven off; it then acquires a dark green colour, and when gently heated, deposits the iridic oxide.—The greater part of the iridic oxide remains on the filter. It is thoroughly washed with water—digested with strong hydrochloric acid, which at first acquires a green colour and gives off chlorine (in consequence of nitric acid still remaining), but afterwards turns brown when the heat rises to the boiling point—after which the residue is well washed, and the filtrate mixed with sal-ammoniac, which precipitates chloriridiate of ammonium in the form of a black crystalline powder. The supernatant liquid, which still contains protochloride of iridium and ammonium, leaves this compound behind when evaporated to dryness. From the two double salts, the iridium is obtained by ignition.—The portion insoluble in hydrochloric acid consists of undecomposed osmium-iridium, insoluble iridic oxide, and silica derived from the porcelain retort. After the latter has been dissolved out by boiling with aqueous carbonate of potash, the residue is pulverized, again fused in the retort with nitre, and treated in the manner just described.

28. *Osmium.* As in *a*, 28.

### C. *According to Fr. Dobereiner and Fr. Weiss.*

(*Ann. Pharm.* 14, 17, and 251.)

1. The platinum ore is heated in a retort with nitric acid, the required quantity being put in at once, and strong hydrochloric acid added by small portions at a time. As soon as the hydrochloric acid present is all decomposed, the liquid begins to jump, which is a sign that more hydrochloric acid is required.

2. The distillate thus obtained is purified by repeated rectification from matter mechanically carried over; it is then nearly neutralized with potash or lime, and heated to the boiling point with formiate of potash. The osmium is thereby precipitated in the form of a blue powder, with evolution of carbonic acid.

3. The solution of the platinum ore (1) is filtered from the undissolved portion, which is then washed; the filtrate and washings, mixed in a dark place and in the cold, with milk of lime, till the liquid is nearly neutralized; after which, lime-water is added in large excess, the liquid filtered as quickly as possible and the filter washed with cold lime-water. All these operations must be performed as far as possible in the dark, at all events only by candle-light. The oxides of the other metals (as Herschel has shown) are precipitated by the lime, but the platinum is not, provided day-light be excluded.

4. The filtrate, which contains all the platinum, together with a little palladium, is immediately mixed with a slight excess of hydrochloric acid, whereby any turbidity that may have been produced by the action of light is removed—and the metals precipitated in a warm place by zinc, till the solution is decolorized. The liquid is then decanted; the zinc freed from adhering platinum by means of a feather and hydrochloric acid; and the platinum washed in the vessel in which it was precipitated, first with dilute hydrochloric acid, then with boiling water, and lastly with nitric acid free from chlorine, to dissolve out the palladium. The platinum then remains in the form of platinum-black.

5. From the nitric acid solution (4), after complete neutralization with carbonate of soda, the palladium is precipitated by cyanide of mercury.

6. The *Platinum*, after being washed with the three liquids as described in (4), is in the form of platinum-black. To free it from charcoal derived from the zinc, it is ignited in a covered crucible so that nothing may be lost by deflagration.

7. The precipitate (3) produced by the lime is dissolved, while yet moist, in hydrochloric acid—the solution, after being nearly neutralized with carbonate of soda, is precipitated by cyanide of mercury—and the liquid filtered.

8. The precipitate (7) consisting of cyanide of palladium and cyanide of copper, is washed on the same filter with the one obtained in (5), after which it is ignited and dissolved in water. The solution is separated by filtration from any charcoal that may be present; nearly neutralized with carbonate of soda; and heated in a capacious vessel with formiate of potash and a small quantity of acetic acid, the formiate of potash being added as long as it causes an evolution of carbonic acid. The *Palladium* then separates in large shining laminæ, while the copper remains in solution.

9. The liquid filtered from the cyanide of palladium (7), together with the wash-water, is mixed with sal-ammoniac and evaporated to dryness. The pulverized residue is then repeatedly digested in alcohol of sp. gr. 0·833, which does not dissolve out any chlororhodiate or chloriridiate of ammonium, as long as chloride of iron is still present. The alcoholic solution contains cyanide of mercury, together with sesquichloride of iron and traces of chloride of copper.

10. The residue is washed with alcohol and digested with hydrochloric acid to dissolve out the iron, and the rhodium separated from the iridium by fusion with bisulphate of potash, according to the method of Berzelius. (p. 261, No. 17.)

11. The portion of the platinum ore which is insoluble in aqua-regia is treated with ammonia to dissolve out any chloride of silver that it may contain. (No particular method is given for the further treatment of the alloy of osmium and iridium; but in this part of the process also, formiate of potash might be useful for the reduction of the osmium.)

*Methods specially adapted for separating the Platinum.*

*a.* Descotils (*Mém. d'Arcueil*; also *Gilb.* 27, 231; *comp.* Hess, *J. pr. Chem.* 40, 498) gradually adds 1 pt. of platinum ore to 4 parts of zinc in a state of fusion; covers the crucible; exposes it to a powerful heat in a wind-furnace, the draught of which is strengthened by putting a high dome upon it; takes the crucible out after half an hour; reduces the

greyish white, somewhat granular alloy to a fine powder; and dissolves out the zinc with oil of vitriol diluted with three times its weight of water, heat being applied towards the end of the process. When the dilute sulphuric acid no longer exerts any action, nitric acid is likewise added to it, and finally the alloy is sometimes treated with hot oil of vitriol; this, however, and the nitric acid dissolve a little platinum and palladium as well as the zinc. The finely pulverized residue thus purified from zinc, and then washed and dried, deflagrates with a hissing noise when heated, but after being washed with hydrochloric acid, no longer exhibits this phenomenon. After washing, it requires to dissolve it only 4 times the quantity of strong aqua-regia (consisting of 1 pt. nitric and 3 pts. hydrochloric) that was used to dissolve the platinum ore. It is best to pour all the nitric acid upon it at first, and then add the hydrochloric acid in small portions. The solution is separated by decantation from the black residue (osmium-iridium); evaporated to dryness; dissolved in water, which leaves behind all the gold in the metallic state; then mixed with cyanide of mercury, which throws down cyanide of palladium; filtered; and mixed with carbonate of soda free from potash and not in excess, which throws down sesquioxide of iron, while the chloroplatinate of sodium which is formed and remains in solution, is not decomposed. The iron precipitate is separated from the platinum-solution by filtration, or better by decantation, and thoroughly washed. Should it contain platinum, that metal is precipitated from the solution in hydrochloric acid by sal-ammoniac. The liquid containing the chloroplatinate of sodium, which should contain a slight excess of acid, and should be neither too concentrated nor too dilute, is mixed with a sufficient quantity of carbonate of soda to give it a slightly alkaline reaction, and then exposed for some time to the air—most advantageously at a temperature between 50° and 60°—whereupon it deposits the iridium in the form of a green precipitate, from which the liquid is separated by filtration. This liquid saturated when cold with hydrochloric acid, and mixed with sal-ammoniac, deposits nearly pure chloroplatinate of ammonium, which is washed with a small quantity of water. (The small quantities of platinum and iridium which remain in the liquid, are precipitated by liver of sulphur.) As a large quantity of platinum is mechanically carried off during the ignition of the chloroplatinate of ammonium, the best method is to ignite it, after thorough drying, in an earthen retort. The spongy platinum is well boiled with water and then with dilute sulphuric acid, afterwards washed with water, re-dissolved in aqua-regia, and precipitated by sal-ammoniac. The chloroplatinate of ammonium thus obtained yields, on ignition, perfectly pure platinum.

*b.* Ridolfi (*Schw.* 24, 39) fuses the ore with lead, then with sulphur, &c.

*Special processes for the treatment of the residue insoluble in aqua-regia.* (*Osmium-iridium.*)

*a. According to* Wöhler (*Pogg.* 31, 161; also *Ann. Pharm.* 9, 149; further *Jahresber.* 15, 147).

1. The residue need not be pulverized, but the coarser grains of osmium-iridium may be picked out. Ammonia is then poured upon the residue to dissolve out the chloride of silver, which, at all events, is produced in the working of the American ore. The residue, after drying, is mixed with an exactly equal weight of decrepitated common salt, and the mixture heated to low redness in a long, wide glass tube. Through

one opening of this tube, undried chlorine gas is slowly introduced, the other end passing into an empty receiver, from the tubulure of which, the chlorine gas, which remains uncombined, together with the vapours of osmic acid, is conveyed by means of a bent tube into aqueous ammonia. In this manner, chloriridiate of sodium and chlorosmiate of sodium are produced, while the titanate of iron remains unaltered. The osmium-salt is decomposed by the moisture of the chlorine gas, into hydrochloric acid and osmic acid, which volatilize, and metallic osmium and chloride of sodium, which remain behind; with these latter substances, the chlorine again forms chlorosmiate of sodium, which is again decomposed, &c.; so that, ultimately, the greater part of the osmium volatilizes in the form of osmic acid, while a small portion sublimes at the colder end of the tube in the form of green or red chloride of osmium. If the chlorine be gradually evolved, it is wholly absorbed, and when, after a few hours, bubbles of it pass over into the ammonia, we may know that the process is at an end. In an experiment performed by Joss (*J. pr. Chem.* 4, 371) in which the chlorine was too rapidly evolved, chloride of nitrogen was formed; he therefore recommends the use of carbonate of soda instead of aqueous ammonia; Berzelius recommends an aqueous solution of potash.

2. The ammoniacal liquid, coloured yellow by osmic acid, is mixed with sal-ammoniac and carbonate of soda, and evaporated to dryness, the residue gently ignited in a retort, and then digested in water to dissolve out the soluble salts, whereupon the osmium is left behind in the form of a black powder. In a similar manner, the sublimed osmic acid may be dissolved in aqueous ammonia, and treated as above. Or if it be preferred to preserve the osmic acid as such, the receiver may be corked and gently heated to the melting point of the acid, and the fused product poured into a well-closed bottle, or into a glass tube which is afterwards hermetically sealed. These operations, however, must be performed with the greatest caution, on account of the injurious action of the osmic acid vapour on the eyes and respiratory organs.

3. The tube (1), together with its slightly aggregated contents, is placed in water; and the deep brown aqueous solution—which smells of osmic acid, produced by the decomposing action of the water on the chloride of osmium—is separated from the insoluble portion, and distilled to half its bulk in order to volatilize the osmic acid, which is then taken up by the aqueous ammonia in the receiver, and reduced as in (2).

4. The liquid (3), remaining in the retort, is filtered, and the filtrate, which contains chloriridiate of sodium, and neither palladium nor rhodium, is evaporated, with gradual addition of carbonate of soda, whereupon a brown precipitate is at first produced, and afterwards a brown-black one. The whole is then evaporated to dryness; the black mass gently heated in a hessian crucible; the residue digested in hot water, which takes up chloride of sodium, carbonate of soda, and a small portion of chromate; and the insoluble residue of black, pulverulent sesquioxide of iridium, which still contains a large quantity of soda, together with small quantities of iron, osmium, and platinum, is washed and dried. The sesquioxide of iridium is reduced by hydrogen gas, and at a high temperature, to ensure complete reduction (although the reduction takes place, with incandescence, even at ordinary temperatures); and the iridium is freed from soda by water, from iron by strong hydrochloric acid, and then from platinum by aqua-regia. The iridium, together with the filter, is then inclosed within a considerable number of folds of paper, and pressed hard into a cake in a screw-press; after which it is dried and exposed to a

violent heat in a blast-furnace. The iridium then remains in the form of a grey, tolerably compact mass, susceptible of polish.

5. The residue (3), insoluble in water, weighs from 25 to 30 per cent. less than the original (impure) osmium-iridium. It is contaminated with a small quantity of metallic osmium, proceeding from the decomposition of the chloride of osmium by water. To purify it further, it is again mixed with common salt, which need not exceed half its weight, then treated with chlorine, &c., whereby it still loses from 5 to 7 per cent. of osmium, iridium, and iron.

Berzelius considers this mode of treating the osmium-iridium as the easiest and most advantageous of all.

*b. According to* Persoz (*Ann. Chim. Phys.* 55, 210; also *J. pr. Chem.* 2, 473).

1. A mixture of 1 pt. of osmium-iridium, 2 parts of dry carbonate of soda, and 3 parts of sulphur, is put into a red-hot earthen crucible, which is heated to whiteness for a few minutes with the cover on, then taken out of the fire, and broken to pieces when cold. Three layers are found within it; at the bottom, a metallic-looking, crystalline mixture of metallic sulphides, also containing sulphide of sodium;—in the middle, pure sulphide of sodium, intermixed with a few crystals of the lower mass; and at top, a brownish crust of silicate [probably also titanate?] of soda.

2. The two lower layers are together treated with water, and the insoluble matter separated from the dissolved portion by subsidence and decantation, and washed in the same manner with water. The water principally holds sulphide of sodium in solution; but also, according to Fr. Weiss & Fr. Döbereiner (*Ann. Pharm.* 14, 16), a considerable quantity of sulphiridiate and sulphosmiate of sodium, which give it a deep grass-green colour, and are precipitated green by acids.

3. The undissolved portion consists of the sulphides of iridium, osmium, iron, and perhaps also platinum. The iron is extracted by dilute hydrochloric acid, and the graphite-like residue, consisting of the sulphides of iridium and osmium, is washed and dried, then mixed with three times its weight of mercuric sulphate, and heated to strong redness in an earthern retort provided with connecting tube and receiver, which causes a copious evolution of sulphurous acid.

4. In the neck of the retort is found a compound of osmic oxide with mercury [mercuric oxide?]; it is gently heated in a slightly inclined glass tube, through which a stream of hydrogen is passed; mercury then volatilizes, and metallic osmium remains behind.

5. In the connecting tube there is found a blue liquid containing osmium, sulphur, and oxygen. By treating it with water, it is converted into a blue powder, which is washed, dried, and, as in (4), reduced by hydrogen to the state of metallic osmium, water and sulphuretted hydrogen being at the same time evolved.

6. The iridic oxide remains in the retort, and is reduced to the metallic state by hydrogen gas at a high temperature. The osmium, which is sometimes, though rarely, mixed with the iridic oxide, may be removed by fusion with hydrate of potash in a silver crucible, and subsequent washing with water, which then extracts osmiate of potash.

(The osmium-iridium is almost completely disintegrated by ignition with pentasulphide of sodium, so that, after being well washed with water, it may be almost wholly oxidized by ignition with 1 part of carbonate of

potash and 2 parts of nitre, and may then be treated with water, dilute nitric acid, and lastly, with hydrochloric acid. *Fr. Weiss & Fr. Dobereiner.*) —*Comp.* Fellenberg (*Pogg.* 41, 210; 44, 220).

*c. According to* Frémy (*Compt. Rend.* 18, 144).

The osmium-iridium is ignited in a crucible with three times its weight of nitre—whereby, according to Frémy, only a small quantity of osmium is volatilized; the fused mass, after an hour's ignition, is poured out upon a plate, the face being covered to protect it from the vapours of osmic acid; the portion soluble in water, distilled with nitric acid; and the osmic received in an aqueous solution of potash. The residue in the retort is digested in water to free it from nitric acid, and the iridic oxide which remains, is dissolved in hydrochloric acid. On the addition of sal-ammoniac to the filtrate, chloriridate of ammonium is precipitated, mixed with chlorosmiate of ammonium. Sulphurous acid gas passed through water in which the precipitate is diffused, converts only the iridium-salt into a soluble salt, which separates from the sal-ammoniac solution in large brown crystals; and these, when ignited in a current of hydrogen, yield metallic iridium.

[For Claus's method of separating *Ruthenium* from the osmium-iridium, see Chap. XLIII.]

*Processes for rendering Platinum malleable.*

The platinum which remains on igniting chloroplatinate of ammonium and similar compounds, has the form of a dull, grey, soft, spongy powder. To convert this substance into malleable platinum, it must be either fused or welded together. For the fusion of platinum *per se*, the heat of the oxy-hydrogen blowpipe, or of Marcet's blowpipe, is required; hence, it is very seldom resorted to on the large scale.—Formerly, Jeanety fused 3 pts. of platinum ore with 6 parts of arsenious acid and 2 of pearl-ash, whereby the base metals were converted into slags; ignited the cast plates of arsenide of platinum under the muffle till the arsenic was burnt away; and hammered together the remaining mass, which had become porous from loss of arsenic.—Similarly, Pelletier recommended for this purpose the addition of a small quantity of phosphorus, and Mussin-Puschkin combined the platinum with mercury, and ignited the amalgam under continued pressure. More recently, these methods have been entirely superseded by that of Wollaston, in which the platinum is welded together without any addition.

*a.* Wollaston's *Process* (*Phil. Trans.* 1829, 1; also *Schw.* 57, 69; also *Pogg.* 16, 158).

The chloroplatinate of ammonium to be used must be as free as possible from chloriridiate of ammonium. It is well washed with cold water, then dried, and heated gently in a black-lead crucible, not more strongly than is necessary to expel the sal-ammoniac, so that the spongy platinum may be left, not in a closely aggregated, but in a loose state. It is rubbed to powder in the gentlest manner between the hands, pressed through a linen bag, and the coarser particles which remain in the bag are triturated in a wooden mortar with a wooden pestle,—not with any harder substance, because the platinum would then acquire the metallic lustre, and would not weld so completely as in the contrary case. The powder is

finally triturated with water, and the finer particles separated from the coarser by elutriation. The whole of the finer powder is then mixed up with water to a uniform paste, and pressed into a brass cylinder. This cylinder is $6\frac{3}{4}$ inches high, 1·12 inch in diameter at top, and 1·23 at bottom; its lower and wider end is accurately closed with a steel stopper, which enters it to the depth of $\frac{1}{4}$ of an inch, and is wrapped round with bibulous paper, by which the running off of the water is facilitated. The interior of the cylinder is smeared with grease, and the cylinder being placed in a glass full of water, is itself filled with water, and then completely filled with the platinum paste. In this manner, all cavities and inequalities are avoided. On the platinum paste is laid, first a piece of blotting-paper, then a layer of woollen cloth, and part of the water is pressed out of it by means of a wooden cylinder held in the hand. A plate of copper is then laid upon the paste, so that the cylinder may be introduced in a horizontal position into a very powerful lever-press, in which a stamp presses on the copper plate. After the pressure, the steel stopper, which closes the lower end of the cylinder, is taken out, and after it the now solid cake of platinum. This cake is heated to redness to drive off the remaining water and the grease, and render it more compact. It is then placed in an air-furnace having a very strong draught and fed with good coke, and exposed for 20 minutes to an intense heat, which is diminished during the last 5 minutes. In the furnace, the cake is laid by one of its ends on a plate of refractory clay strewn with pure quartz-sand and placed $2\frac{1}{2}$ inches above the grate, and a cylindrical pot is inverted over it in such a manner as not to touch the platinum at any point. The cake, while still red-hot, is taken from the furnace, laid down on one of its bases, and struck repeatedly on the other with a heavy hammer. Should it bend, it must not on any account be hammered on the side, as that would break it, but must be straightened by well-directed blows on the ends. When the cake has been sufficiently condensed by this treatment, it may be brought into any required form by heating and hammering, just like any other ductile metal. If the platinum has become covered, while in the fire, with ferruginous scales, it must be coated with a moist mixture of equal measures of borax and cream of tartar; heated to redness in an air-furnace on a platinum tray, over which an earthen pot is inverted; and immersed, while still hot, in dilute sulphuric acid, which dissolves the flux in a few hours.—Specific gravity of the cake (with its interstices), after pressure, about 10·0; after strong ignition, from 17·0 to 17·7; after hammering, 21·25; after drawing out into thick wire, 21·4; and after drawing out into very thin wire, 21·5. (Wollaston.)

### *b. Russian Process for the Coinage of Platinum.*

The spongy platinum is triturated dry in a brazen mortar with a brazen pestle; the powder sifted through a fine sieve; introduced dry into a cast-iron cylinder; and strongly compressed by a steel die, under a powerful screw-press. The cylinder is then taken out of the mould; ignited in a pottery-furnace for a day and a half, during which the height diminishes by $\frac{1}{3}$ and the diameter by $\frac{3}{16}$; and is thereby converted into perfectly malleable platinum. (Sobolewski, *Pogg.* 33, 99; also *Ann. Pharm.* 13, 42; *comp.* Marshall, *Phil. Mag. Ann.* 11, 321.)

For the formation of small platinum crucibles, &c., the steel mortar described by Abich (*Pogg.* 23, 309) may be used. The platinum powder

may be introduced into it, either dry or moist; the stamp driven in by means of a press, or if that be not at hand, by repeated blows of a hammer; the platinum cylinder then forced out by removing the piece which closes the lower end of the mortar, and carefully pressing the stamp further inwards; and the cylinder ignited in a crucible, first gently in an air-furnace, then more strongly in the blast-furnace, and beaten on the anvil while still red-hot. (Gm.)

Jacquelain (*Ann. Chim. Phys.* 74, 213; also *J. pr. Chem.* 22, 22) precipitates a solution of 100 parts of platinum in aqua-regia with a mixed solution of 25 pts. chloride of potassium and 36 pts. sal-ammoniac; dries the precipitate well, and introduces it into a red-hot platinum crucible by small portions at a time, as the reduction goes on; ignites it more strongly for 20 minutes after the whole has been introduced; washes the spongy mass, first with water containing hydrochloric acid (to remove any ferric oxide that may be present), then with pure boiling water, till all the chloride of potassium is dissolved out; heats the platinum, consisting of fine, soft, easily welding laminæ, to redness; introduces it while still red-hot, into a heated, polished, cast-iron cylinder, fastened by its base to a wooden block which serves as a support; places upon it a polished cylinder which fits well into the outer one; strikes the upper cylinder first with light but afterwards with heavy blows, by means of a rammer; takes out the cake, ignites it again, and presses it once more in the cylinder.

It has also been proposed to reduce platinum (in the same manner as copper) by the electrotype process. (*Phil. Mag. J.* 18, 442.)

*Properties of Platinum.*—Platinum united in compact masses is harder than copper, but softer than iron. By loading platinum wires with weights, it is found that platinum exceeds all metals in tenacity, excepting iron and copper. After gold and silver, it is the most ductile of the metals, and may be drawn out into extremely thin wires. Alone, it may be drawn out to the thickness of $\frac{1}{1940}$ of an inch; but when enclosed within a silver wire (I. 409), it may be reduced to $\frac{1}{5000}$ and even to $\frac{1}{30000}$ of an inch in thickness; in the latter case, however, the wire is not coherent in long pieces. (Wollaston, *Ann. Phil.* 1, 224; also *Gilb.* 52, 284.) It may also be beaten out into very thin laminæ, like gold-leaf. (Klingenstein, *Kastn. Arch.* 14, 162.) A small proportion of iridium makes it harder and less ductile.—Specific gravity of hammered platinum 20·857 (Clarke), 20·98 (Borda), 21·061 (Sickingen), 21·25 (Faraday & Stodart; Wollaston), 21·45 (Berzelius), 21·74 (Klaproth), 23·543, at 17° (Cloud); of platinum united by welding and drawn out into thick wire, 21·4; when drawn out into very thin wire, 21·5; of platinum fused by the oxygen-gas blowpipe and drawn out into wire, 21·16 (Wollaston).—Platinum may be welded at a white heat. On this property is founded Wollaston's process for giving coherence to platinum (p. 271), also that of Marx, for repairing injured platinum vessels (p. 275).—It does not fuse *per se* in the strongest heat of a forge. According to Faraday and Stodart, it fuses imperfectly: if however the fuel be not kept from contact with it, fusion takes place from formation of an alloy of silicium and platinum.—Fuses in an alcohol flame fed with oxygen gas, in the flame of the oxy-hydrogen blowpipe, in the focus of a large burning glass, and in the circuit of Children's galvanic battery.

Platinum possesses the following advantages over other metals as a material for chemical vessels: 1. It withstands oxidation in the air at a

red heat as well as gold and silver, and is, at the same time, much harder and more difficult of fusion.—2. It is not attacked either by sulphur or by mercury.—3. It does not dissolve in any simple acid, so that nitric acid and oil of vitriol may be boiled in it; in aqua-regia, likewise, it dissolves much less readily than gold.—To prevent injury to platinum vessels, the following precautions must be observed: They are attacked by chlorine-water, by mixtures of hydrochloric acid with nitric acid or chromic acid and their salts, also with peroxide of manganese and other peroxides. No metal must be heated in them to a temperature near its melting point, because it will then form a fusible alloy with the platinum and perforate the vessel. This effect is produced with especial facility by arsenic, antimony, tellurium, bismuth, zinc, cadmium, tin, lead, and, at higher temperatures, also by copper and silver.—A similar effect is produced by the oxides of these metals, also by the salts of arsenic and antimonic acid, if any substance be present which can take up their oxygen, such as organic acids, the charcoal of filters, bits of charcoal accidentally dropping in, or even the carbonic oxide gas of the charcoal or coke fire, especially at a white heat, at which temperature the oxides of nickel, cobalt and copper may likewise do injury.—The same danger is incurred in fusing phosphoric acid and certain phosphates in platinum vessels, inasmuch as by the action of the carbon, an easily fusible phosphide of platinum is formed.—When the sulphide or cyanide of an alkali-metal is fused in a platinum crucible, a considerable quantity of platinum is taken up by it.—When a platinum crucible is ignited in an open charcoal fire, silicium reduced from the charcoal-ash gets access to it and makes it brittle and disposed to crack.—When potash-hydrate or nitre is ignited in a platinum vessel, the metal is slowly oxidized, but more quickly than silver or gold, with formation of platinate of potash; similarly with soda, and still more with lithia.—Phosphoric acid may be fused in clean platinum vessels, provided all reducing agents be kept away, the metal not becoming brittle till after more than 1000 fusions. But if the platinum contains arsenic, as is the case with that prepared by Jeanety's process, it is attacked by phosphoric acid prepared from phosphorus by the action of nitric acid, though not by that which is obtained from bone-ash by sulphuric acid. The vessel first acquires a blue tarnish, and is afterwards corroded, even to perforation. At the same time, the fused phosphoric acid turns yellow, becomes covered with a metallic film, which afterwards disappears and imparts a brown colour to the acid; and the aqueous solution of the acid, when treated with sulphuretted hydrogen, yields sulphide of platinum together with sulphide of arsenic. (Stieren, *Repert.* 39, 1.)—Gay-Lussac & Thénard (*Récherches*, 1, 292) observed that platinum crucibles are quickly perforated when boracic acid containing sulphuric acid is fused in them. Probably their crucibles also contained arsenic; at all events, the author has frequently performed this fusion without any injury to the crucibles.—To test platinum vessels, they should be boiled first with hydrochloric acid, then with dilute nitric acid, and an examination subsequently made of the acids, to ascertain whether they have dissolved anything, and if so, what is its nature. (Stieren.)

To clean platinum crucibles which have been used, from adhering oxide of iron and other impurities, they may be smeared with a mixture of equal measures of pounded borax and cream of tartar made into a paste with water—ignited till the flux fuses—and then immersed for several hours in dilute sulphuric acid, which dissolves the flux. (Wol-

laston.) Or the crucibles to be cleaned may be placed one within the other—a little bisulphate of potash put into each—the whole heated for a while, so that the fused mass may surround the crucibles within and without—and then washed with water. (Gm.)

Perforated and otherwise injured platinum vessels may be repaired by welding. The requisite conditions are: A bright surface, a strong red heat, and moderate hammering. If the surface is not clean, it must be scraped bright and smooth with the sharp edge of a file, but must not be polished. Moreover, the surface must be quite free from iron-spots and rust, and should therefore not be struck with an iron hammer. Perfect welding requires a white heat, but platinum surfaces begin to adhere together at a red heat. While the union is being brought about by hammering, the pieces must be at least at a red heat. Only moderate blows must be given, not strong enough to beat the metal out. A succession of short, firm strokes, given as quickly as possible after the metal has been taken out of the fire, is most effective. Small pieces of the metal are heated before the blowpipe or the glass-lamp upon charcoal, larger pieces, in the forge.—To mend a crack at the edge of the crucibles, a narrow bent piece of platinum-foil is suspended over the crack and pressed close—the crucible bound round at the lower part with iron wire—then put into the fire with a pair of tongs—thence, when white-hot, transferred to the pointed end of the anvil, and subjected to moderate blows with a broad, smooth hammer. If the welding is not complete, the operation must be repeated.—When a crucible is perforated with a small hole, the end of a platinum wire of proper thickness is passed through, beaten flat at the end, nipped off with the pliers on the other side, and beaten out there also. This rivet, when heated to whiteness, welds firmly under the hammer.—To mend larger holes, a piece of platinum-plate of proper size is beaten out, and fastened with one or more rivets, for which holes have been previously bored. After proper welding the join is no longer visible. (Marx, *Schw.* 66, 159.)—(It had previously been stated by Wollaston (*Pogg.* 16, 160), that a platinum wire cut through obliquely with a sharp tool, and joined together by the cut surfaces, may be readily welded together under the hammer at a red heat, but that the union would not take place, or but imperfectly, if the cut surfaces had been previously polished.

*Platinum-Deposits on Glass:*

*a.* When bichloride of platinum is gently heated with alcohol, a brown mass is obtained, which readily chars when heated. On dissolving this mass in alcohol, dipping a glass into the solution, turning it about in several directions so that the liquid may diffuse itself uniformly over it, and then heating the glass to redness over a spirit-lamp, a shining deposit of platinum, which cannot be rubbed off, is left upon it. But in contact with zinc and dilute sulphuric acid, it immediately separates in delicate, transparent laminæ. (Döbereiner, *Schw.* 54, 414.)

*b.* The aqueous solution of platinate of potash or soda, mixed with one-fourth of its volume of alcohol, then introduced into a graduated glass tube, and exposed to sunshine, deposits the whole of the platinum in a film of such extreme thinness, that the glass tube still appears transparent and merely turbid. In this tube, detonating gas quickly condenses; it may be used several times as a eudiometer over water (but not over mercury), without losing its efficiency. (Döbereiner, *Kastn. Arch.* 9, 341.)

¶ According to Lüdersdorf, a specular deposit of platinum (*platinum-lustre*) may be formed on all glazed surfaces, and therefore both on porcelain and on glass, by dissolving bichloride of platinum which has been evaporated to dryness without decomposition, in alcohol of 95 or 96 per cent., and slowly pouring the solution into five times its bulk of oil of lavender. Protochloride of platinum is thereby produced, and remains dissolved, in consequence of the simultaneous formation of acetic or hydrochloric acid. With vessels having a lead-glazing, the burning-in takes place at a low red-heat; with porcelain and glazings free from lead, at a bright red heat.—The method formerly adopted for producing platinum-lustre on earthenware, was by means of an emulsion of platinum-solution and linseed-oil; it was applicable only to glazes containing lead. (Lüdersdorf, *Dingl. pol. J.* 105, 36.) ¶

*Platinum-Deposits on Copper and Brass:*

The copper or brass, previously cleaned with sand and hydrochloric acid, is immersed for a few seconds in a boiling solution of 1 pt. chloroplatinate of ammonium and 8 sal-ammoniac in 32—40 parts of water, till a sufficient deposit is formed upon it—after which it is cleaned with prepared chalk, and then washed and dried. (Böttger, *Ann. Pharm.* 39, 175.)

[Respecting platinum-deposits formed by galvanic action, *vid.* (I. 500, 501). For the observations of Bromeis on *Plating with Platinum* on silver, copper and brass, *vid. Jahrsber. L. & K.* 1850, 631.]

Platinum exhibits two states of minute division. In *Spongy Platinum*, which is formed at a red-heat, the metal is finely divided, but in the crystalline state; and in *Platinum-black*, which is produced at ordinary temperatures, it is amorphous.

*a. Spongy Platinum:*

Generally obtained by igniting the chloroplatinate of ammonium. To obtain this compound as free as possible from other metals—which would otherwise remain mixed with the spongy platinum, and weaken its action in setting fire to hydrogen gas, &c. (*e. g.*, in Döbereiner's Instantaneous Light Machine)—the methods already described for the decomposition of platinum ore may be adopted; viz., those of Berzelius (p. 264, Process *b*, No. 7—12), and of Döbereiner & Weiss (p. 266, 3 and 4), excepting that the liquid filtered from the lime-precipitate must be slightly acidulated with hydrochloric acid, immediately precipitated by sal-ammoniac, and completely freed from chloride of calcium by washing. (The wash-water of the precipitate formed by lime is concentrated by evaporation after the addition of hydrochloric acid, before it is precipitated by sal-ammoniac. (*N. Br. Arch.* 14; 274.)—Spongy platinum is a dull grey, soft, porous substance, having the same specific gravity as massive platinum. The more strongly it is ignited, the more closely do its particles unite. By pressure with a hard body, it is condensed into laminæ having the metallic lustre.—Its action on gases and vapours mixed with oxygen has been specially described in Vol. II., pp. 49, 50.

*b. Platinum-black*:

This form of platinum, with its remarkable action on oxygen gas and combustible bodies, was discovered by Edm. Davy, who, however, was led by certain small accidental impurities to regard it as nitrite of platinous oxide, till Liebig showed that pure platinum-black consists of pure finely divided platinum.

*Preparation.* 1. When alloys of platinum with other metals are treated with acids which attack the foreign metals but not the platinum, the former are dissolved out, and the platinum remains in the form of a black powder, having the properties of platinum-black. *a.* In this manner it was obtained by Descotils (p 267), who remarked the hissing which it makes when heated. [According to Boussingault, this black powder also contains 31 per cent. of zinc. *Vid. Platinum and Zinc.* But Boussingault omitted the use of nitric acid and oil of vitriol.]—A powerful platinum-black is obtained by fusing 1 pt. of platinum ore with 2 parts of zinc; pulverizing the alloy, and treating it first with sulphuric and then with dilute nitric acid, till the whole of the zinc is dissolved, which takes place but slowly; separating the residual alloy, by elutriation with water, from the heavier grains of osmium-iridium; and then washing it with potash-ley, and afterwards with water. Since the platinum-black thus obtained is still mixed with the osmium and iridium of the ore, it transfers to the osmium the oxygen which it takes from the air, converting that metal, soon after drying, into osmic acid, which may then be separated by distillation with water. (W. Döbereiner, *Ann. Pharm.* 17, 67.)—*b.* The author likewise found that an alloy of pure platinum with copper and zinc, when treated with nitric acid, left the platinum in the form of platinum-black.—*c.* When a mixture of aqueous bichloride of platinum and sesquichloride of iron is precipitated by ammonia, the washed and dried precipitate reduced at a red heat by hydrogen gas, and the resulting alloy of platinum and iron treated with hydrochloric acid to dissolve out the iron, there remains a black powder, which, when heated in open vessels to a temperature considerably below redness, takes fire and detonates slightly, but not in close vessels; it is not raised to a red heat by contact with alcohol. (Berzelius.) (According to Boussingault, this powder contains 19·9 per cent. of iron; *vid. Platinum and Iron.* In that place, also, will be found a description of a similar powder obtained by Faraday & Stodart.) —*d.* Platinum fused with potassium, separates out in black scales when the alloy is immersed in water. (Berzelius.) These two substances obtained by Berzelius consist of platinum-black. They set fire to alcohol; thus *d* produces this effect, if it be previously freed from adhering hydrochloric acid by washing with potash and water. (W. Döbereiner.)

2. Platinum-black is also formed by precipitating platinum from its solutions with zinc.—The solution of bichloride of platinum, to yield the black, must contain free hydrochloric acid, and be dilute; from a more neutral solution, zinc precipitates the platinum in grey, coherent lumps. (Liebig.)—The precipitate thrown down by zinc from a platinum solution (p. 267, No. 4), after being freed from palladium by nitric acid, then washed with water, boiled with potash-ley, and again washed, appears denser than platinum precipitated in other ways, absorbs less oxygen, and consequently does not set fire to alcohol; hence it is best adapted for converting that compound into acetic acid. (Fr. Döbereiner, *Ann. Pharm.* 14, 259; *comp.* W. Döbereiner, *Schw.* 54, 414.) Another mode of preparation is to reduce chloroplatinate of ammonium or potassium immersed in hydrochloric acid, by zinc, and free the resulting platinum-black from zinc by nitric acid. (Berzelius.)

3. By precipitating aqueous bichloride of platinum with hydrosulphuric acid, washing the precipitated sulphide of platinum, and exposing it for some weeks to the air. By this process, oxidized sulphide of platinum is formed. (W. Döbereiner, *Schw.* 54, 414.) [Since, as stated by

Berzelius, moist sulphide of platinum, when exposed to the air, forms a quantity of sulphuric acid, sufficient to blacken the paper on which it rests, it is possible that oxidized sulphide of platinum may be merely metallic platinum separated from the sulphide and mixed with sulphuric acid.]

4. By reducing platinum with an organic compound.—*a.* By *Formic acid.*—Aqueous bichloride of platinum mixed with formiate of soda. (Göbel.) Or platinate of soda heated with aqueous formic acid. (W. Döbereiner, *Pogg.* 28, 181.)

*b.* By *Tartaric acid.* Cooper (*Qu. J. of Sc.* 5, 120), by mixing aqueous bichloride of platinum with tartrate of soda, at temperatures between 82° and 93°, obtained a greyish-black powder, which he supposed to be hydrated platinic oxide; it shrank together to $\frac{1}{8}$ of its bulk at a red heat, and was converted into ductile platinum.—This precipitate, washed and dried at 100°, gives off only 1·41 per cent. of hygroscopic water at a red heat, and must be regarded as platinum-black. The same precipitate is obtained with tartrate of potash, ammonia, or lime, at a boiling heat, and moreover with evolution of carbonic acid, but not with free tartaric acid or cream of tartar; at ordinary temperatures, tartrate of potash throws down chloroplatinate of potassium. (R. Phillips, *Phil. Mag. J.* 2, 94.)

*c.* By *Alcohol.* *a.* Edm. Davy's original process (*Schw.* 31, 240): Sulphide of platinum, precipitated from the solution of the bichloride by sulphuretted hydrogen, is converted into sulphate of platinic oxide by boiling with nitric acid, and the solution mixed with an equal quantity of alcohol. The liquid then becomes perfectly colourless, after several days at ordinary temperatures, but immediately on heating; and there is formed a black precipitate, which must be washed with water. This precipitate, when heated, yields several products (*vid. inf.*), among which is hyponitric acid. (E. Davy.) But if the precipitate be previously boiled with potash and then with water, it still retains its peculiar properties, but gives off no nitrous gas; the presence of nitrogen-compounds in it is therefore accidental. (Liebig, *Pogg.* 17, 102.)—*β.* Protochloride of platinum is heated in a retort provided with a receiver, with 12 times its weight of alcohol, of sp. gr. 0·813. It turns black, while the colourless alcoholic liquid becomes sour, and gives off vapour of hydrochloric ether. The liquid is poured off, and the black substance washed and dried. This body, when heated, even out of contact of air, deflagrates with a hissing noise, and exhibits a glimmering light, giving off oxygen, carbonic acid, and water. (Zeise, *Pogg.* 9, 632.) When hydrogen gas is passed over this preparation, it becomes heated to redness, yielding, however, not water, but hydrochloric acid; it therefore contains a chlorine-compound accidentally mixed with it. (Liebig, *Pogg.* 17, 102.)—*γ.* Bichloride of platinum is exposed to a continued strong heat, till it is for the most part converted into the protochloride; the portion which remains undecomposed is extracted with hot water; the insoluble protochloride is heated in a flask with strong potash-ley till completely dissolved; and the black liquid removed from the fire, and gradually mixed, while still hot, with alcohol. A large quantity of carbonic acid is then disengaged, with strong effervescence, together with an ethereal substance, and the platinum-black falls to the bottom in the form of a very heavy powder, which must be washed, first with a small quantity of alcohol, then with hydrochloric acid, then with potash, then 4 or 5 times with water, and after thoroughly washing, dried in a porcelain basin, without bringing it

in contact with the filter or any other organic substance. If a large quantity of cupric nitrate be added to the solution of protochloride of platinum in potash, before boiling it with the alcohol, the platinum-black will be mixed with twice its weight of copper, but will be quite as active as when pure. (Liebig, *Pogg.* 17, 101; abstr. *Mag. Pharm.* 29, 101.)—δ. 3 parts of hydrate of potash are dissolved in 12—18 parts of boiling brandy; 4 parts of chloroplatinate of potassium added to the solution in a wide glass vessel; and the vessel set aside for 8 days, in a warm place, where it is exposed to the rays of the sun (the liquid being frequently stirred), till all the platinum is precipitated, and no more gas-bubbles rise from the liquid on stirring. If, during this process, the liquid should cease to exhibit an alkaline reaction, more potash must be added to it, for the alkali must always be kept in excess. The potash, in fact, combines with the acetic acid produced from the alcohol, by the oxygen of that part of the potash to which the chloride of platinum gives up chlorine. The liquid is decanted, and the platinum-black washed, first with pure water, then with water containing acetic acid, then again with pure water, and dried upon bibulous paper. When large octohedrons of chloroplatinate of potassium are treated in this manner, a platinum-black is obtained possessing the highest degree of inflaming power. (W. Döbereiner, *Ann. Pharm.* 2, 1.)—Another method is to expose a solution of platinum in aqua-regia, supersaturated with potash and mixed with a little alcohol, to the sun, till all the platinum is precipitated in the form of black. In this case, if the solution still contains nitric acid, a very large quantity of ammonia is evolved towards the end of the process; but its formation ceases, as soon as all the platinum is reduced to the form of black. (W. Döbereiner, *Schw.* 63, 476.)—ε. The aqueous solution of bichloride of platinum is mixed first with acetate of soda, then with alcohol. (W. Döbereiner, *Pogg.* 28, 181.)

*d.* With *Sugar.* The aqueous solution of 4 parts of bichloride of platinum is mixed with 10 to 12 parts of crystallized carbonate of soda and 1 part of sugar, and heated to 100° over the water-bath, with constant agitation, till, in the course of a quarter or half an hour—the liquid having previously acquired a dark-brown colour—the whole of the platinum is precipitated in the form of black; the liquid is then decanted, when cold, and the platinum-black washed with water and dried. This process is the most convenient and economical of all, but it succeeds only when the platinum-solution is free from nitric acid. The black which it yields sets fire to alcohol as quickly as that of E. Davy. (W. Döbereiner, *Ann. Pharm.* 2, 1.)

In whatever manner platinum-black is prepared, it is well to boil it with nitric acid, to remove foreign metals, then with potash-ley, and finally with water. (W. Döbereiner, *Ann. Pharm.* 14, 17.)

Platinum-black is a soft, black, dull-looking powder, which soils any surface on which it is rubbed. (E. Davy.) Granular and rough to the touch: of sp. gr. from 15·78 to 16·32 and 17·572. By pressure, it acquires a white colour and metallic lustre. Inodorous. (Liebig.) Platinum-black obtained from platinate of soda and formic acid, is not pulverulent, but consists of extremely fine laminæ. (Döbereiner.) G. Rose found the specific gravity of platinum-black prepared in different ways, to vary from 16·83 to 22·89; in one specimen, it was only 14·89. (*Jahresber.* 1847—8, 38.)

If platinum-black be completely freed from alcohol by boiling with

water, then dried in vacuo over oil of vitriol, and the air afterwards quickly admitted to it, such abundant absorption [of oxygen gas?] takes place, that the substance becomes heated to redness, and the paper in which it is enveloped burns away. (Liebig.)

Liebig's platinum-black, when heated to redness in the air, in oxygen, or in hydrogen gas, loses nothing in weight, exhibits no incandescence, and in hydrogen gas, does not form water.—During the process of drying, the black absorbs a large quantity of oxygen from the air, but no nitrogen, or at most an extremely small quantity. At a red heat, it might be expected to give up the oxygen; but instead of that, it evolves carbonic acid, sometimes, but not invariably, mixed with oxygen. For it always contains carbon, even when precipitated by zinc, that metal, in fact, never being free from carbon. Thus, 60 grains of platinum-black prepared with zinc, in which, according to the quantity of carbonic acid gas which it yields with formic acid, there should be contained 1·26 cubic inches of oxygen, give off at a red heat, not this quantity of oxygen, but 1·20 cubic inches of carbonic acid, together with a trace of water. (W. Döbereiner, *Ann. Pharm.* 14, 10.)

Many kinds of platinum-black deflagrate with a hissing noise when heated, even much below redness. That which is obtained from the alloy of platinum and zinc, by the method of Descotils and Döbereiner (1, *a*), sometimes detonates like gunpowder (Descotils); that which is prepared from the alloy of platinum and iron (1, *c*), exhibits hissing deflagration when gently heated in an open vessel, but not in a close vessel. (Berzelius.)—Edmund Davy's platinum-black (4, *c*, *a*), which contains 96·25 per cent. of platinum and 3·75 of nitrous acid, oxygen, and carbonic acid, deflagrates when heated, with a hissing noise and red flame, and yields platinum; if heated out of contact of air, it gives off carbonic acid, oxygen, water, and hyponitric acid, and leaves platinum. (E. Davy.)—May not this deflagration be due to the presence of considerable quantities of carbon, alcohol, or other compounds of carbon in these kinds of platinum-black? Thus, Liebig found that his platinum-black, when dried in vacuo, still retained alcohol (which could only be driven off by continued boiling with water), and consequently took fire at 100°.

Platinum-black, by means of the oxygen which it has absorbed, exerts an oxidizing action upon most combustible gases and vapours, both organic and inorganic, whereby it may itself be heated to redness, and if the air has access to it, may set the gases on fire. If access of air or of oxygen gas be prevented, this oxidation ceases as soon as the oxygen absorbed by the platinum-black is consumed (even in this case, however, the black, if not moist, may be raised to a red heat in hydrogen gas); but if the air or oxygen has access to it, the platinum-black takes up more oxygen, which it transfers to the combustible body; and thus the action becomes continuous. (W. Döbereiner; *comp.* II., 51; see also *Oxalic acid*, *Formic acid*, *Marsh gas*, *Olefiant gas*, *Ether*, *Alcohol*, *Wood-spirit*, and *Cyanogen*.) The more strongly and frequently platinum-black is heated to redness by its action on combustible gases, the denser does it become, and the more nearly does it approach in its properties and activity to spongy platinum.—It loses its activity in ammoniacal gas, and when moistened with hydrochloric acid; but recovers it on being moistened with aqueous potash or carbonate of soda, and subsequently dried, the ammonia then escaping. The activity of platinum-black is also destroyed by moistening it with aqueous bichloride of platinum and alcohol at the

same time, but may be restored by continued washing with carbonate of soda, and subsequent drying. Sulphuric and nitric acid do not impair its activity. (W. Döbereiner.)

Edmund Davy's platinum-black likewise exhibits the following properties: In dry ammoniacal gas, it rises to a red heat, with decrepitation and emission of sparks, and absorbs a large quantity of the gas. When agitated with aqueous ammonia, whereby gas-bubbles are evolved, it acquires detonating properties. Heated with phosphorus, it forms phosphide of platinum, with vivid combustion; and when heated with sulphur, yields blue sulphide of platinum. (E. Davy.)

## *Compounds of Platinum.*

### Platinum and Oxygen.

### A. Platinous Oxide. PtO.

*Protoxide of Platinum, Platinoxydul.*—Appears to be formed in the combustion of platinum, which takes place at the melting-point of the metal, and is attended with sparkling, with emission of fumes, and formation of a dingy green dust. The combustion does not take place at an ordinary white heat, but only in the flame of hydrogen gas burning in contact with oxygen, or of a spirit-lamp fed with oxygen gas, or when a strong voltaic or electrical battery is discharged through thin platinum wires.

*Preparation.* 1. By carefully heating the hydrate of platinous oxide till it is deprived of its water. (Berzelius.)—2. When Herschel's platinate of lime is strongly ignited in a covered crucible, a dark violet powder is obtained, which becomes very hot by contact with water, and, when freed by water and nitric acid from chloride of calcium and lime, leaves a residue of platinous oxide. (Döbereiner, *Pogg.* 28, 183.)

*Properties.* Prepared by (1): grey (Berzelius); by (2): dark violet. (Döbereiner.)

| | | | |
|---|---|---|---|
| Pt ..... | 99 | ..... | 92·52 |
| O ..... | 8 | ..... | 7·48 |
| PtO ..... | 107 | ..... | 100·00 |

(PtO = 1233·499 + 100 = 1333·499. Berzelius.)

*Decompositions.* Reduced to the metallic state at a red heat; detonates strongly when heated to redness in contact with charcoal powder. (Berzelius.)—By aqueous formic acid, it is reduced to platinum-black, with violent evolution of carbonic acid. (W. Döbereiner.)

*Combinations.* *a.* With Water.—Hydrate of Platinous Oxide, or Platinous Hydrate.—Prepared by decomposing protochloride of platinum with a gently heated solution of potash, and washing the precipitate. Part of the protoxide remains dissolved in the potash, forming a dark green solution, from which it may be precipitated by sulphuric acid. (Berzelius.) The hydrate thus obtained cannot be completely freed from chlorine; if too much potash be added, the precipitate re-dissolves. (Liebig, *Pogg.* 17, 108.) If the hydrate be separated from the protochloride by soda, a very considerable portion of soda remains in it, after

washing with water, and is left behind with the platinum, on ignition. (Vauquelin.)—Bulky, black powder.—When heated, it gives off water and afterwards oxygen; boiling hydrochloric acid resolves it into aqueous bichloride of platinum and a residue of metal; boiling potash-solution, into soluble platinate of potash and metallic platinum. (Berzelius.)

*b.* With Acids, it forms the Salts of Platinous Oxide, or Platinous Salts.—The violet oxide obtained by (2), does not dissolve in any oxygen-acid, excepting sulphurous acid; when boiled with aqueous oxalic acid, it takes up the latter. (Döbereiner.)—Some platinous salts are dark brown and red, others colourless. When ignited, they leave metallic platinum. Hydrosulphuric acid and hydrosulphate of ammonia colour their solutions brown, and, after a while, throw down a brown-black precipitate of protosulphide of platinum, soluble in a large excess of hydrosulphate of ammonia, and forming a brown-red solution. Iodide of potassium colours them deep red-brown, and after a while, decolorizes the liquid, and forms a black, metallic-looking precipitate. Protochloride of tin colours the solutions deep red-brown, without forming any precipitate. Mercurous nitrate produces a black precipitate. Ammonia added in excess to the hydrochloric acid solution, throws down green crystalline ammonio-protochloride of platinum. Carbonate of potash or soda produces a brownish precipitate, which is slowly deposited, the liquid retaining a brown-red colour.—The following substances have no action on platinous salts: potash, carbonate of ammonia, phosphate of soda, oxalic acid, cyanide of mercury, ferrocyanide of potassium, and ferricyanide of potassium. (H. Rose, *Analyt. Chemie.*)

*c.* With Ammonia, platinous oxide forms two peculiar salifiable bases; it also combines with potash and soda.

By mixing a solution of bichloride of platinum diluted with hot water, with a solution of mercurous nitrate made as neutral as possible, Cooper obtained a yellowish-brown precipitate (probably consisting of calomel and platinic oxide), which, when gently heated to a temperature short of redness, was resolved into volatile calomel and a residue of black oxide containing 95·764 platinum and 4·235 oxygen. The amount of oxygen appears, however, to vary with the degree of heat. (Berzelius, Phillips, *Ann. Phil.* 22, 198.)

When fulminating platinum is boiled down to dryness with strong nitric acid, the residue heated nearly to redness, and the remaining oxide pulverized, boiled with water and aqueous potash, to free it from the obstinately adhering nitric acid, and then dried at the boiling-point of mercury, it exhibits a dark steel-grey colour and metallic lustre; contains 89·37 metal, and 10·63 oxygen; gives off its oxygen at a strong red heat; is decomposed, with vivid incandescence, when heated with zinc-foil, yielding platinum and oxide of zinc; forms sulphide of platinum and sulphurous acid when heated with sulphur; and dissolves only in hot hydrochloric acid, not in cold hydrochloric acid, boiling nitric acid, or aqueous alkalis. (Edm. Davy, *Schw.* 31, 353.)—Is this a mixture of the protoxide and bi-oxide, or is it a peculiar intermediate oxide?

¶ *Blue Oxide.*—According to Hittorf (*Pogg.* 74, 316), platinum immersed, as the negative pole of a voltaic battery, in fused nitrate of potash, forms a blue oxide, a blue liquid at the same time flowing continuously from the metal; this blue oxide, however, as it leaves the platinum, passes into yellow and green oxide, which remain suspended in the nitrate of potash; when the liquid cools, and attracts moisture, the green oxide changes into the yellow. In nitrate of soda, the oxidation is

weaker, and the blue colour lighter and finer; moreover, the blue oxide then changes only to yellowish brown. ¶

## B. Platinic Oxide. $PtO^2$.

*Bioxide of Platinum, Platinoxyd. — Formation.* Platinum is not oxidized by water, sulphuric acid, or nitric acid. It is converted into hydrochlorate of platinic oxide when treated with aqua-regia or chlorine-water, though the latter acts upon it but slowly; it is likewise oxidated by ignition with hydrate of potash, hydrate of lithia, or carbonate of lithia, provided the air has access to it—and by ignition with nitre.

*Preparation.* By gently heating the hydrated oxide. (Berzelius.)

*Properties.* Black powder. (Berzelius.)

| | | | Berzelius. | Chenevix. | Richter. |
|---|---|---|---|---|---|
| Pt | 99 | 86·09 | 85·93 | 87 | 89·3 |
| 2O | 16 | 13·91 | 14·07 | 13 | 10·7 |
| $PtO^2$ | 115 | 100·00 | 100·00 | 100 | 100·0 |

($PtO^2 = 1233{\cdot}499 + 200 = 1433{\cdot}499$. Berzelius.)

When heated, it gives off oxygen, and leaves metallic platinum.

*Combinations. a.* With Water.—Hydrate of Platinic Oxide, or Platinic Hydrate.—1. From most platinum-salts, alkalis throw down basic double salts; but from nitrate of platinic oxide, potash throws down at first the pure hydrate, which may be separated, and afterwards the double salt. (Berzelius.)—2. The hydrate may also be obtained by precipitating a hot solution of platinic sulphate with carbonate of lime, dissolving out the excess of that substance from the precipitate by means of acetic acid, and then washing it for a long time [to remove the gypsum]. (Wittstein, *Repert.* 74, 43.)—3. By dissolving out the soda from platinate of soda, with acetic acid. (Döbereiner, *Pogg.* 28, 181; also Frémy, *Compt. rend.* 31, 893.)—The hydrate (1) when recently precipitated, has a rusty colour, like that of hydrated ferric oxide; in drying, it shrinks together into a yellowish-brown mass. When heated, it gives off water, and turns black. (Berzelius.)—(2) is an umber-brown powder, which does not decompose at 100°, but at a stronger heat, is resolved, with explosion and scattering of part of the mass in the form of a blackish fume, into aqueous vapour, oxygen gas, and platinum. (Wittstein.)

| | | | Wittstein. |
|---|---|---|---|
| Pt | 99 | 74·44 | 73·98 |
| 2O | 16 | 12·03 | 26·02 |
| 2HO | 18 | 13·53 | |
| $PtO^2$,2HO | 133 | 100·00 | 100·00 |

*b.* With Acids, forming the Salts of Platinic Oxide, or Platinic Salts.—From bichloride of platinum (or hydrochlorate of platinic oxide), obtained by dissolving platinum in aqua-regia, then freed by evaporation from excess of acid, and again dissolved in a small quantity of water, several other platinic salts may be prepared, by adding a compound of potash with another acid, as long as a precipitate of chloroplatinate of potassium is produced—evaporating the decanted liquid—and dissolving the residue in a small quantity of water, which still leaves behind a certain quantity of chloroplatinate of potassium. (Berzelius, *Pogg.* 1, 436.)

Platinic salts have a yellow or brown colour, redden litmus, and have an astringent taste. They yield metallic platinum when ignited, but impart no colour to fluxes. From their aqueous solutions, phosphorus and most metals precipitate metallic platinum. The reduction of platinum from the solution of the chloride is much slower than that of gold. It is most quickly reduced by zinc, cadmium, iron, cobalt, and copper. The platinum coats the metals in the form of a black powder, which gradually reunites into laminæ; part of it, however, especially when the precipitating metal is iron or copper, is deposited in the metallic state on the neighbouring glass surface.—Nickel, mercury, and bismuth reduce it more slowly; the precipitate produced by bismuth exhibits the metallic lustre. Tin reduces it quickly, but the portion of that metal which dissolves, forms with the undecomposed platinum-salt, a brown-red compound, which remains in solution.—Lead reduces the platinum somewhat quickly at first, and the precipitate exhibits the metallic lustre; but after a while, the deposit of chloride of lead puts a stop to the action.—Silver acts in the same manner, but much more slowly.—Antimony in the first few days merely acquires a grey tarnish, but gradually reduces the whole of the platinum.—Arsenic becomes covered somewhat quickly with a black powder, and darkens the colour of the liquid, but does not effect a complete reduction, even if immersed in the solution for months.—Tellurium precipitates the platinum very slowly, in the form of a black powder.—Palladium produces but a very slight precipitate (Selenium exerts no reducing action). (Fischer, *Pogg.* 9, 256; 10, 607; 12, 505.)—Many organic compounds reduce platinum from the solution of the chloride, in the form of platinum-black. This effect is produced by the alkaline formiates, tartrates, and racemates, with the aid of heat, also by alcohol and sugar, after the addition of potash or carbonate of soda.—The alkaline oxalates, citrates, acetates, and benzoates, exert no reducing action. (Brandes, *Ann. Pharm.* 9, 302.)

Hydrosulphuric acid produces at first only a brown colouring, but after a while, a brown precipitate of sulphide of platinum. The same precipitate is produced by hydrosulphate of ammonia, and dissolves in a large excess of that reagent.—The limit of this reaction is found when 1 pt. of platinum is dissolved in 30,000 pts. of liquid; the precipitate is soluble in hydrochloric acid. (Fischer, *Schw.* 53, 108.)—1 part of bichloride of platinum dissolved in 100 parts of water to which 25 parts of hydrochloric acid are added, is not precipitated by hydrosulphuric acid. (Reinsch, *J. pr. Chem.* 13. 132.)—Free trithionic acid forms a black precipitate in platinum-solutions. (Langlois.)—Hydriodic acid colours them red-brown, and after two days, throws down metallic platinum in flakes. (Silliman, *Sill. Am. J.* 6, 326.)—Iodide of potassium colours them deep brown-red, throws down a brown precipitate (of iodide of platinum), and on the application of heat, produces a metallic deposit on the sides of the vessel. (H. Rose.) 1 pt. of platinum, dissolved in the form of chloride in 10,000 parts of water, produces, on the addition of iodide of potassium, first an orange-yellow, then a red colour; with 20,000 parts of liquid, a yellow colour is produced in a few minutes, and afterwards a red; with 40,000, yellowish at first, rose-coloured afterwards; with 80,000, still distinctly rose-coloured; with 160,000, rose-coloured after a few minutes; with 320,000, a scarcely perceptible rose-colour appears after some time. (Lassaigne, *J. Chem. méd.* 8, 585.)—1 pt. of chloride of platinum in 10,000 parts of water, produces a brown-red colour with iodide of potassium, afterwards a dark-green colour, and finally a black precipitate;

larger quantity of liquid, a red colour is produced, still distinguishable in 1,000,000 parts of water, but not beyond. (Walcker, *N. Quart. J. of Sc.* 3, 378.)—Protochloride of tin produces a dark, red-brown colouring, and after a while, a gelatinous precipitate, having the same colour, the liquid at the same time becoming colourless. In a dilute solution, protochloride of tin produces a yellow colour and yellow precipitate, which dissolves in hydrochloric acid, producing a brown solution. The limit of the colouring is found with 1 pt. of platinic oxide in 100,000 pts. of liquid; for this reaction, an acid tin-solution, which keeps the precipitate dissolved, is more delicate than a neutral solution. (Fischer, *Schw.* 53, 108.) 1 pt. of platinum (as chloride) dissolved in 10,000 pts. of liquid, forms with protochloride of tin, a reddish-yellow liquid and a precipitate; in 20,000 pts. of liquid, a paler reddish-yellow colour without a precipitate; with 40,000, an orange-yellow; with 80,000, yellowish; with 160,000, pale yellow; and with 640,000, a very pale yellow colour. (Lassaigne, *J. Chim. méd.* 8, 585.)—Mercurous nitrate produces a deep reddish-yellow precipitate with chloride of platinum. Platinum sal-ammoniac dissolved in 100,000 parts of water, immediately imparts a yellow colour to the mercurous solution, and soon after forms a yellow precipitate; when the quantity of water amounts to 200,000 parts, a distinct yellow colour is still produced after a few minutes. (Böttger, *Schw.* 68, 292.)—When free hydrochloric acid is present in the solution, ammonia, carbonate of ammonia, and other ammoniacal salts, throw down a lemon-yellow, crystallo-pulverulent precipitate of platinum sal-ammoniac, not perceptibly soluble in acids, but soluble in a large quantity of water.—In a similar manner, caustic potash, carbonate of potash, and other potash-salts, precipitate chloroplatinate of potassium, of similar aspect and properties. Carbonate of soda, on the contrary, forms no precipitate at ordinary temperatures, but, on the application of heat, a brownish-yellow precipitate of platinate of soda.

Platinic salts are not precipitated by phosphuretted hydrogen gas (thereby distinguished from palladium), (Böttger); by green vitriol (which distinguishes them from silver, gold, and palladium); by phosphate of soda, oxalic acid, infusion of galls, ferrocyanide and ferricyanide of potossium (excepting that when free hydrochloric acid is present, a small quantity of chloroplatinate of potassium may be precipitated); or by cyanide of mercury (which again distinguishes them from palladium).

*c.* With all Alkalis, forming compounds called *Platinates.*

## Platinum and Carbon.

Carbide of Platinum.—Platinum may be fused in contact with charcoal in the blast-furnace (Chenevix, Descotils, *Ann. Chim.* 67, 89); when thus treated, however, it appears to take up silicium rather than carbon (vid. *Silicium and Platinum*). Platinum vessels ignited over an alcohol flame increase very slightly in weight, an effect probably due to the formation of carbide of platinum; *e. g.* a capsule weighing 3 ounces gained 6 grains in 10 years. (Fischer, *Kastn. Arch.* 14, 148.) When platinum is heated to redness over a simple alcohol flame, a black powder is deposited where the interior of the flame comes in contact with the metal, and this powder, when burned away, leaves a small quantity of platinum.

When chloroplatinite of mesityl ($C^3H^5O$,PtCl) is gradually heated to

redness in a retort, and then left to cool out of contact of air, a black residue of $PtC^2$ is obtained, which exhibits no free platinum under the magnifying glass, and when heated in the air, burns slowly away, leaving metallic platinum. Heated aqua-regia dissolves out the greater part of the platinum from it, and leaves 12·29 per cent. of charcoal still containing platinum. (Zeisé, *J. pr. Chem.* 20, 209.)

| | | | | Zeise. |
|---|---|---|---|---|
| Pt..... | 99 | .... | 89·19 | ..... 88·878 |
| 2C ..... | 12 | .... | 10·81 | ..... 11·122 |
| $PtC^2$..... | 111 | .... | 100·00 | ..... 100·000 |

## Platinum and Boron.

*Boride of Platinum?*—Platinum, heated with borax and charcoal, fuses into a hard, brittle, somewhat crystalline mass, which, when dissolved in aqua-regia, leaves a residue of boracic acid. (Descotils, *Ann. Chim.* 67, 88.)

## Platinum and Phosphorus.

Phosphide of Platinum.—*a.* By fusing platinum with glacial phosphoric acid and charcoal powder, or by throwing pieces of phosphorus on red-hot platinum, Pelletier obtained from 100 parts of platinum, 128 parts of phosphide of platinum, which was white, very brittle, and very fusible; gave sparks on steel; crystallized in cubes; and when heated in the air, parted with its phosphorus by combustion.

*b.* Phosphorus heated with spongy platinum in a glass tube exhausted of air, combined with it at a heat considerably below redness, producing flame and vivid incandescence, and formed a lead-grey, porous, imperfectly fused mass, partly crystallized in cubes, and a non-conductor of electricity. It contained 82·5 platinum and 17·5 phosphorus. When heated in chlorine gas, it was converted into terchloride of phosphorus and chloride of platinum; and when heated with chlorate of potash, it was partly decomposed with incandescence. (E. Davy.)

*c.* 3 parts of chloroplatinate of ammonium and 2 parts of phosphorus heated to dull redness in a tube closed with mercury, formed an iron-black, partly pulverulent, partly loosely coherent mass, having scarcely any metallic lustre, of sp. gr. 5·28, and a non-conductor of electricity. It contained 70 platinum and 30 phosphorus; was permanent in the air; but slightly attacked by mineral acids, even at a boiling heat; decomposed in chlorine gas, like *b*; detonated with chlorate of potash under the hammer; and corroded platinum at a white heat. (E. Davy.)

## Platinum and Sulphur.

A. Protosulphide of Platinum, or Platinous Sulphide.—1. Formed by mixing spongy platinum with an equal weight of sulphur, and heating the mixture nearly to redness in a glass tube exhausted of air. (E. Davy.) —2. By igniting chloroplatinate of ammonium with twice its weight of sulphur in a closed crucible. (Vauquelin.)—3. By heating the same salt with an equal weight of sulphur and ignited carbonate of soda, and afterwards dissolving out the sulphide of sodium by water. (Vauquelin.)

4. By igniting oxidized sulphide of platinum (p. 289, *b*) in a platinum crucible till it takes fire with a loud hissing noise; closing the crucible well, and leaving it to cool; boiling the residue with aqua-regia, to remove any bichloride of platinum that may adhere to it; and washing and drying in vacuo. (Böttger, *J. pr. Chem.* 3, 274.)—5. By decomposing protochloride of platinum with an alkaline hydrosulphate. (Berzelius.)—Prepared by (1): Dull, lead-grey powder, of sp. gr. 6·2; acquires the metallic lustre when rubbed upon paper, and is a non-conductor of electricity; by (2): shining black powder; by (3): slender, black, shining needles (Vauquelin); by (4): blue-black, sandy to the touch, grates between the fingers; sp. gr. 8·847 (Böttger). Heated to redness in a close vessel, it undergoes a kind of fusion. (Vauquelin.)

| | | | | Böttger. (4) | E. Davy. (1) | Vauquelin. (2) | (3) |
|---|---|---|---|---|---|---|---|
| Pt | 99 | 86·09 | | 85·51 | 84 | 84·5 | 83·5 |
| S | 16 | 13·91 | | 14·49 | 16 | 15·5 | 16·5 |
| PtS | 115 | 100·00 | | 100·00 | 100 | 100·0 | 100·0 |

Leaves metallic platinum when heated to redness in the air. Decomposed by ignition with zinc-filings or chlorate of potash. When exposed to a current of hydrogen gas at a temperature of only 19°, it becomes red-hot, and is reduced to spongy platinum, with formation of hydrosulphuric acid. (Böttger.) Permanent in air and in water; scarcely attacked by mineral acids at a boiling heat. (E. Davy.) Not decomposed even by boiling aqua-regia or caustic potash. Acts upon alcohol in the air like platinum-black, but much less strongly. (Böttger.)

B. Bisulphide of Platinum, or Platinic Sulphide.—1. Formed by mixing 3 parts of chloroplatinate of ammonium with 2 parts of sulphur, heating the mixture to low redness over a spirit-lamp in a glass tube closed with mercury, and removing the heat soon after the evolution of gas has ceased. (E. Davy.) Böttger is of opinion that the compound thus prepared is contaminated with free sulphur, in consequence of not being heated long enough.—2. By precipitating a platinic salt with hydrosulphuric acid or an alkaline hydrosulphate. The compound may be formed either by passing hydrosulphuric acid gas through aqueous chloroplatinate of sodium, or by dropping aqueous bichloride of platinum into an alkaline hydrosulphate (for hydrosulphuric acid forms, with aqueous bichloride of platinum, a precipitate which contains chloride of platinum, and detonates when heated). The precipitate is washed with boiling water and dried in vacuo. (Berzelius.)—3. A solution of 1 part of dry bichloride of platinum in 4 parts of absolute alcohol is mixed with 5 parts of bisulphide of carbon in a strong wide-mouthed bottle (the mixture filling two-thirds of it); and the bottle, after being tightly closed and shaken, is set aside in a shady place of medium temperature, and agitated again after 24 hours, by which time the mixture has acquired a black-brown colour. In the course of a week, it solidifies in a black gelatinous mass, having an ethereal odour. This mass is twice washed with alcohol of 80 per cent., to remove the bisulphide of carbon, then rubbed quickly to a pasty consistence, and boiled with a large quantity of water in an evaporating basin (stirring constantly), whereupon a gas is evolved which burns with a blue flame on the application of a light. The mass is then thrown on a filter, and washed with water, till the liquid which runs through no longer forms a cloud in a silver-solution; and the filter, with its contents, is quickly freed, by pressure between bibulous

paper, from the greater part of the water, and quickly dried in vacuo over oil of vitriol at a temperature below 125°. (Böttger, *J. pr. Chem.* 3, 267.)

Prepared by (1), it is a dark steel-grey, often coherent powder; on paper, it forms a dark metallic streak like native sulphide of antimony; it is soft to the touch, of specific gravity about 3·5, a non-conductor of electricity, and infusible. (E. Davy.)—By (2): dark brown, black after drying. (Berzelius.); black and shining. (Fellenberg, *Pogg.* 50, 70.)—By (3): blackish grey powder, with shining points, sandy to the touch, and grates between the teeth; its specific gravity is 7·224, and it is a good conductor of electricity. (Böttger.)

| | | | E. Davy. | Vauquelin. | Fellenberg. | | Böttger. |
|---|---|---|---|---|---|---|---|
| | | | (1) | (2) | (1) | (2) | (3) |
| Pt ..... | 99 | 75·57 | 72 | 77 | 75·31 | 74·63 | 75·11 |
| 2S ..... | 32 | 24·43 | 28 | 23 | 24·69 | 25·37 | 24·89 |
| $PtS^2$..... | 131 | 100·00 | 100 | 100 | 100·00 | 100·00 | 100·00 |

The preparation (1) leaves metallic platinum when ignited in contact with air. (E. Davy.)—(2) gives off 1 At. sulphur at commencing redness, and leaves protosulphide of platinum. (Berzelius.) Decomposition begins between 225° and 250°. (Böttger.) The preparation (1) decomposes when fused with chlorate of potash, heated with zinc, or fused with hydrate of potash. (E. Davy.)—(3) is likewise decomposed by fusion with hydrate of potash, chlorate of potash, or nitre; but to decompose it completely, repeated ignition is required. (Böttger.) Chlorine gas decomposes (1) and (2) at an incipient red heat, the products being chloride of sulphur and metallic platinum. (Fellenberg.) Potassium, kneaded together with (3) at ordinary temperatures decomposes it with intense combustion; sodium does not act till heated. (Böttger.) Among the acids, hot aqua-regia alone exerts a slight action upon this compound. (E. Davy.) Fuming nitric acid decomposes and dissolves (3) slowly, but completely; so likewise does boiling aqua-regia, and with greater facility. The preparation (2), exposed in the moist state to the air, produces sulphuric acid, which chars the paper on drying. (Berzelius.) According to Böttger, a similar effect is exhibited by (3); *vid. inf.*—(2) dissolves completely in alkaline hydrosulphates; caustic alkalis also dissolve it with separation of platinum and formation of alkaline hyposulphites. (Berzelius.)

The preparation (1) is not decomposed by air at ordinary temperatures, by water, or by simple acids. (E. Davy.) The following substances exert no decomposing action on (2): hydrogen gas at ordinary temperatures; boiling concentrated hydrochloric or sulphuric acid, or nitric acid of specific gravity 1·2; boiling aqueous ammonia, potash, carbonate of soda, and hydrosulphate of ammonia. (Böttger.)

When 1 pt. of platinum ore is heated to incipient whiteness with 2 parts of carbonate of soda and 3 parts of sulphur, and the fused mass exhausted with water, sulphide of platinum remains in long aurora-red needles. (Persoz, *Ann. Chim. Phys.* 55, 215.) No analysis is given.

When hydrosulphuric acid gas is passed through sulphide of platinum precipitated by (2) the sulphide acquires a red-brown colour by absorbing the gas, but gives it up on exposure to the air, and becomes black again. (Berzelius.)

*Oxidized Sulphide of Platinum.—a.* When bisulphide of platinum obtained according to (2) by hydrosulphuric acid gas, is exposed to the

air while still moist, a large quantity of sulphuric acid is formed in it. (Berzelius.) [In this case, the platinum appears to transfer the oxygen of the air to the sulphur, in the same manner as it does to hydrogen, &c.]—This mass [which must contain a considerable quantity of free platinum] exhibits similar actions to other kinds of platinum-black.—*b.* When bisulphide of platinum prepared by (3) is dried, not in vacuo, but exposed to the air in a capsule at a temperature between 50° and 62°, and constantly stirred, till it is converted into a very fine powder, and afterwards heated to 100° in a small retort, a velvet-black powder is obtained, dotted with a few light points; its specific gravity is about 6·286; it contains 60·22 per cent. of platinum, has a very sour taste, and yields a large quantity of sulphuric acid when treated with water. It takes fire in an open crucible at 250°, burning with a hissing noise and violet flame, and continues to glow, with evolution of sulphurous acid. If a stream of hydrogen gas be allowed to act upon it at a temperature above 25°, it becomes warm, after glowing and decrepitating, gives off sulphuretted hydrogen, and leaves spongy platinum. (Böttger.)

C. *Sulphite of Platinous Oxide,* or *Platinous Sulphite?* — Platinous oxide prepared by method 2 (p. 281), dissolves easily and abundantly in aqueous sulphurous acid. The colourless solution, which, if prepared out of contact of air, contains neither sulphuric nor hyposulphuric acid, leaves, on evaporation, a colourless, gummy salt, which reddens litmus. At a red heat, this salt is resolved into oil of vitriol and metallic platinum. It is not decomposed, either by hydrochloric or by sulphuric acid. It dissolves easily in water and alcohol. Its aqueous solution, mixed with protochloride of tin, acquires a dark brown-red colour, and gives off a large quantity of sulphurous acid. From an aqueous solution of chloride of gold, it throws down metallic gold, with formation of sulphuric acid and bichloride of platinum.—The salt forms, with various sulphites, colourless double salts, which are permanent in the air and sparingly soluble. (Döbereiner, *J. pr. Chem.* 15, 315.)—From the quantitative determination of the product resulting from the decomposition by chloride of gold, Döbereiner assigns to the salt the formula $PtO^2,2SO^2$.—Should it not be $PtO,SO^2$? The latter supposition is corroborated by the want of colour in the salt, and by the circumstance that bioxide of platinum is reduced to protoxide by sulphurous acid; moreover, the violet preparation used by Döbereiner is, according to his former statement (*Pogg.* 28, 183), not bioxide, but protoxide of platinum, as indeed it should be, according to its mode of preparation.—Platinous oxide [prepared by (1) ?], diffused in water through which sulphurous acid gas is passed, dissolves slowly in the liquid; and carbonate of soda added to the greenish-brown solution, throws down sulphite of platinous oxide and soda. (Litton & Schnedermann, *Ann. Pharm.* 42, 319.)

D. Sulphate of Platinous Oxide, or Platinous Sulphate.—1. Hydrated platinous oxide, precipitated from its solution in potash by sulphuric acid, and washed, dissolves in dilute sulphuric acid after the saline liquid has been decanted off, and forms a dark brown solution, which assumes a redder tint on dilution with water, and, as the platinous oxide takes up more oxygen, gradually becomes clearer. (Berzelius.)—2. When protochloride of platinum is continuously heated with a large quantity of oil of vitriol, till the liquid no longer produces any turbidity in a silver-solution, and the liquid is subsequently evaporated, a black,

uncrystallized mass is obtained, which deliquesces in the air, and forms a black solution with a small quantity of water, but yellowish-green with a larger quantity. This solution becomes darker at first on the addition of potash or soda, but loses its colour in a few days, and deposits hydrated platinous oxide. (Vauquelin.)—The dark brown solution of platinous sulphate deposite metallic platinum at a certain degree of concentration. (Litton & Schnedermann.)

E. Sulphate of Platinic Oxide, or Platinic Sulphate.—When pieces of platinum-foil are introduced into a retort in which oil of vitriol is rectified, they acquire a crystalline aspect, and colour the residue in the retort brownish-yellow, by formation of platinic sulphate. (Fischer, *Kastn. Arch.* 14, 149.) [Did the oil of vitriol contain nitric acid?]—*Preparation.*—1. By dissolving hydrated platinic oxide in sulphuric acid.—2. By mixing a solution of bichloride of platinum in a small quantity of water, with the proper quantity of sulphuric acid, and evaporating to dryness. (Berzelius.)—3. By pouring fuming nitric acid on sulphide of platinum precipitated by sulphuretted hydrogen, and evaporating to dryness, then pouring more fuming nitric acid on the residue, and again evaporating to dryness. (E. Davy.)—Black, shining, porous mass, resembling sugar charcoal; tastes sour, metallic, and somewhat sharp; reddens litmus slightly. (E. Davy.)

| | | | | | Berzelius. | | E. Davy. |
|---|---|---|---|---|---|---|---|
| $PtO^2$ | 115 | .... | 58·97 | ..... | 58·777 | ..... | 73·7 |
| $2SO^3$ | 80 | .... | 41·03 | ..... | 41·223 | ..... | 26·3 |
| $PtO^2,2SO^3$ | 195 | .... | 100·00 | ..... | 100·000 | ..... | 100·0 |

At a red heat, it gives off oxygen gas, sulphurous acid, and fuming oil of vitriol, and leaves metallic platinum. (E. Davy.)—Deliquesces quickly in the air; dissolves in water, forming a dark brown solution; also in aqueous phosphoric, hydrochloric, and nitric acid, and in alcohol and ether. (E. Davy.)—Potash added to the aqueous solution, throws down a basic double salt. (Berzelius.) Alkalis do not throw down platinic oxide from it. (Liebig, *Ann. Pharm.* 23, 37.)

F. Sulphocarbonate of Platinum.—$PtS^2,2CS^2$.—Aqueous sulphocarbonate of calcium forms, with platinic salts, a black-brown precipitate, which dissolves in excess of the calcium-salt, forming a brownish-yellow solution. The precipitate, when dry, is nearly black; and when distilled, gives off, first bisulphide of carbon, and then sulphur, and leaves protosulphide of platinum. (Berzelius.)

## Platinum and Selenium.

Selenide of Platinum.—Selenium heated with spongy platinum, unites with it readily, producing vivid combustion, and forms a grey, infusible powder, which, when heated before the blowpipe, gives off all its selenium in the oxidized state. (Berzelius.)

## Platinum and Iodine.

A. Protiodide of Platinum, Platinous Iodide, or Iodoplatinous Acid.—To form this compound, protochloride of platinum, produced by

heating the bichloride and washed with alcohol, is heated for a quarter of an hour with aqueous iodide of potassium, and the resulting black powder is washed and dried. No action takes place in the cold.—Soft, black powder, which sticks to the fingers like lamp-black; it is tasteless, inodorous, and permanent in the air. (Lassaigne.)

| | | | | | Lassaigne (*mean*). |
|---|---|---|---|---|---|
| Pt ..... | 99 | ..... | 44 | ..... | 43·95 |
| I..... ..... | 126 | ..... | 56 | ..... | 56·05 |
| PtI..... | 225 | ..... | 100 | ..... | 100·00 |

When heated to about the boiling point of mercury, it gives off its iodine, and leaves spongy platinum. Potash and soda convert it into platinous oxide, part of which separates in the form of a black powder, while the rest remains dissolved in the alkali, and in the iodide of potassium or sodium. When digested with ammonia, it leaves a dark yellowish-green powder, which consists of platinous oxide, iodide of platinum, and ammonia; and when heated gives off water, ammonia, and hydriodate of ammonia. A cold aqueous solution of hydriodic acid, of sp. gr. 1·038, gradually dissolves biniodide of platinum from it, and leaves metallic platinum. A hot aqueous solution of iodide of potassium acts upon it in a similar manner, dissolving a certain quantity of biniodide of platinum, whereby the liquid acquires a yellow colour, but leaves the greater part of the protochloride of platinum undecomposed.—Concentrated sulphuric, hydrochloric, and nitric acid, and likewise water and alcohol, have no action upon it. (Lassaigne, *J. Chim. méd.* 8, 708; also *Ann. Chim. Phys.* 51, 113.)

B. *Sesqui-iodide of Platinum?*—A dilute aqueous solution of bichloride of platinum is mixed in excess with iodide of potassium, and the resulting precipitate freed from admixed chloroplatinate of potassium by washing with a large quantity of water, and then dried.—Black.—Gives off a large quantity of iodine at 121°, and the whole at a temperature short of redness.—Dissolves in aqua-regia, with separation of iodine. Gives up a small quantity of iodine to boiling water. When immersed in ammonia, it first turns greenish, then brown, then red; the supernatant liquid yields small crystals on evaporation. Dissolves in potash-ley, forming a yellow solution, which becomes pale red when neutralized with nitric acid, and colourless when supersaturated with it. Dissolves readily, with a wine-red colour, in aqueous iodide of potassium, and likewise in hydriodic acid. Cold sulphuric, hydrochloric, and nitric acid, as well as water, alcohol, and ether, have no action upon it. (Kane, *Phil. Mag. J.* 2, 197.)—[Possibly a mere mixture of protiodide and biniodide of platinum, formed from the latter by continued washing with boiling water.]

| | | | | | Kane. |
|---|---|---|---|---|---|
| 2Pt..... | 198 | ..... | 34·38 | ..... | 35 |
| 3I ..... | 378 | ..... | 65·62 | ..... | 65 |
| $Pt^2I^3$ ..... | 576 | ..... | 100·00 | ..... | 100 |

C. BINIODIDE OF PLATINUM, PLATINIC IODIDE, or IODOPLATINIC ACID.—Spongy platinum, heated with dry iodine, combines with it imperfectly; when heated with iodine and water, or with hydrochloric acid and nitric acid, it remains unaltered.—*Preparation.*—1. The aqueous solutions of bichloride of platinum and iodide of potassium form, at ordinary temperatures, a deep red, clear mixture, which becomes brown and turbid

when heated, and deposits the biniodide, either in flakes or in a crystalline powder, according to the concentration of the mixture; the deposit is washed with boiling water and dried. If the platinum-solution contains free hydrochloric acid, vapours of iodine are given off on heating the mixture.—Black powder, resembling charcoal powder; sometimes crystalline like pulverized oxide of manganese; inodorous and tasteless. (Lassaigne.)

| | | | | Lassaigne. |
|---|---|---|---|---|
| Pt ..... | 99 | ..... | 28·21 | ..... 28·09 |
| 2I ..... | 252 | ..... | 71·79 | ..... 71·91 |
| $PtI^2$ ..... | 351 | ..... | 100·00 | ..... 100·00 |

When heated above 131°, it begins to give off iodine, and ultimately leaves metallic platinum. If only part of the iodine be driven off by careful heating, there remains, not protiodide of platinum, but a mixture of platinum with the biniodide.—Chlorine-water dissolves it gradually, forming bichloride of platinum, while the iodine is set free; or, if excess of chlorine is present, forms chloride of iodine. The biniodide is not decomposed by cold oil of vitriol; but when heated with it, gives off iodine just as when heated alone.—Combines with the more basic metallic iodides, forming crystallizable iodine-salts.—Dissolves in alcohol, forming a yellowish-green solution, and undergoing partial decomposition. (*Vide Alcohol.* Lassaigne, *J. Chim. méd.* 5, 334; 8, 712.)

D. Hydriodate of Platinic Iodide.—Cold dilute hydriodic acid, placed in contact with biniodide of platinum for 24 hours, forms a beautiful red solution, which, when evaporated in vacuo, or over lime in a receiver not exhausted, yields crystals.—These crystals are reddish-black needles, having a metallic lustre, and united in feathery tufts; they are inodorous, and have an astringent, and somewhat acid taste.—In a dry vacuum, they slowly evolve a small quantity of hydriodic acid; at 100°, a larger quantity, but not the whole; and, if afterwards more strongly heated, they yield hydriodous acid and iodine, while platinum remains behind. They become slightly moist on exposure to the air, and dissolve very easily in water. The dark wine-red solution diluted with a large quantity of water, gradually deposits the biniodide of platinum; in sunshine, the deposition takes place more quickly. Chlorine decomposes the solution, throwing down iodine and iodide of platinum; alkalis added to it, immediately form iodine-salts. (Lassaigne.)

| | *Crystallized.* | | Lassaigne. |
|---|---|---|---|
| $PtI^2$ ..... | 351 .... | 73·43 ..... | 73·45 |
| HI ..... | 127 .... | 26·57 ..... | 26·55 |
| $PtI^2$,HI .... | 478 .... | 100·00 ..... | 100·00 |

E. Iodate of Platinic Oxide, or Platinic Iodate.—Iodic acid forms, with bichloride of platinum, a yellow precipitate, somewhat soluble in water. (Pleischl.)

## Platinum and Bromine.

A. Bibromide of Platinum, Platinic Bromide, or Bromoplatinic Acid.—Cold bromine has no action upon platinum (Balard); neither does bromine vapour, passed over red-hot platinum wire, exert any action

upon it. (Liebig.)—The compound is formed by dissolving platinum in a mixture of hydrobromic and nitric acid, and evaporating the solution (at 70°, according to Bonsdorff) to dryness. (Balard.)—Brown crystalline mass, whose aqueous solution reddens litmus. (Bonsdorff.)—Resolved into its elements at a red heat. (Balard.)—Deliquescent (Rammelsberg); dissolves in water, forming a reddish-yellow solution. With more basic metallic bromides, which destroy its power of reddening litmus, it forms bromine-salts (*Bromoplatinates*) of a deep red colour. (Bonsdorff, *Pogg.* 19, 343.)

B. Bromate of Platinic Oxide, or Platinic Bromate.—When aqueous platinic sulphate is precipitated by bromate of baryta, a yellow filtrate is obtained, which, when evaporated over the water-bath, soon gives off oxygen gas and bromine vapour, and finally solidifies in the form of brown, crystalline bibromide of platinum. (Rammelsberg, *Pogg.* 55, 86.)

## Platinum and Chlorine.

A. Protochloride of Platinum, Platinous Chloride, or Chloroplatinous Acid.—1. Pulverized bichloride of platinum placed in a porcelain basin standing in the sand-bath, is heated, with constant stirring, to the melting point of tin. (Berzelius.) Vauquelin digests the product with water to extract any bichloride of platinum that may remain undecomposed.—2. If the heat applied be not sufficient to decompose the whole of the bichloride of platinum, the residue dissolves completely in water, forming a dark brown, nearly opaque liquid, because the protochloride of platinum is rendered soluble through the medium of the bichloride. On evaporating the solution, the protochloride is deposited in the form of a brown powder, the quantity being greater, the more the liquid is concentrated; and on evaporating to dryness and digesting in cold water, the whole of the brown powder remains undissolved. This powder, notwithstanding its different colour, has the same composition as the greenish-grey protochloride of platinum, but dissolves much more easily in hydrochloric acid. After the liquid containing the bichloride of platinum has been decanted off, the brown powder is no longer soluble in water, but dissolves again in the decanted liquid, on the application of heat and addition of water. (Magnus, *Pogg.* 14, 239.)—(1.) Greenish-grey powder, which, like a fatty substance, is scarcely wetted by water. (Berzelius.)—(2.) Brown powder. (Magnus.)

| | | | Berzelius. | Magnus. | | Vauquelin. |
|---|---|---|---|---|---|---|
| | | | (1) | (1) | (2) | (1) |
| Pt | 99·0 | 73·66 | 73·3 | 73·62 | 74·05 | 72·5 |
| Cl | 35·4 | 26·34 | 26·7 | 26·38 | 25·95 | 27·5 |
| PtCl | 134·4 | 100·00 | 100·0 | 100·00 | 100·00 | 100 0 |

Decomposed by heat into chlorine gas and platinum. With aqueous potash, it yields hydrated platinous oxide and chloride of potassium; converted by boiling aqua-regia and also by hydrochloric acid, if the air has access to it, into aqueous bichloride of platinum. Not affected by nitric acid, sulphuric acid, or water. (Berzelius.)

B. Hydrochlorate of Platinous Chloride, or Acid Hydrochlo-

RATE OF PLATINOUS OXIDE.—Formed by dissolving protochloride of platinum in strong boiling hydrochloric acid, out of contact with the air. (Berzelius, Vauquelin.) The brown protochloride dissolves much more readily than the grey. (Magnus.) The purple-red solution, when evaporated, leaves the brown protochloride, insoluble in water. Soda throws down from it the black hydrated protoxide. (Vauquelin.)

C. BICHLORIDE OF PLATINUM, PLATINIC CHLORIDE, or CHLOROPLATINIC ACID.—Anhydrous liquid chlorine has no action on platinum wire. (Kemp.) Chlorine-water slowly dissolves platinum.

*Preparation.* 1. By dissolving platinum in concentrated aqua-regia, and evaporating the solution to dryness over the water-bath. To dissolve the platinum, the presence of nitrous acid is required. A mixture of pure nitric acid (free, *i.e.* from nitrous acid) and chlorate of potash, has no action on spongy platinum, even at 125°. Neither is the spongy platinum attacked by a cold mixture of hydrochloric and pure nitric acid sufficiently diluted; but on the addition of nitrite of potash, chloroplatinate of potassium is very slowly produced. (Millon, *Compt. rend.* 14, 906.)—2. By passing chlorine gas through warm water in which chloroplatinate of ammonium is diffused, till the whole of the ammonia is decomposed, and evaporating. (Vauquelin.) In this process, the dangerous chloride of nitrogen is very likely to be formed.

Dark red-brown mass; its aqueous solution reddens litmus, has a very astringent taste, and colours the skin brownish black.

| | | | | Berzelius. | Vauquelin. |
|---|---|---|---|---|---|
| Pt | 99·0 | 58·30 | | 58·01 | 47 |
| 2Cl | 70·8 | 41·70 | | 41·99 | 53 |
| $PtCl^2$ | 169·8 | 100·00 | | 100·00 | 100 |

Berzelius's numbers are calculated from his analysis of chloroplatinate of potassium.—Vauquelin suspects that his chloride of platinum was not quite freed from acid and water.

Gives off chlorine when heated, being first reduced to protochloride of platinum, and then to the metallic state. (Berzelius.) Platinum retains chlorine much more tenaciously than gold; hence if a mixture of the chlorides of the two metals be carefully heated, the undecomposed chloride of platinum may be extracted by water, while metallic gold remains behind. (Gm.) Sulphurous acid gas passed through the aqueous solution of bichloride of platinum, decolorizes it by converting the bichloride of platinum into protochloride; the same effect is produced by alkaline sulphites. A solution of the bichloride through which sulphurous acid gas has been passed for 8 hours, exhibits a dark brown colour, and forms with ammonia the green precipitate ($NH^3$,PtCl) discovered by Magnus; but after boiling or standing for some time, it loses its colour, and then no longer gives a precipitate with ammonia. (Liebig, *Ann. Pharm.* 23, 23.) The solution decolorized by sulphite of ammonia or sulphite of potash is not precipitated by ammoniacal salts or by boiling with potash. When exposed to the air, it recovers its yellow colour. (Liebig, *Pogg.* 17, 108.) The application of heat to the platinum-solution saturated with sulphurous acid, accelerates the decoloration; the sulphites of ammonia and potash act in the same manner as free sulphurous acid, but an excess of them produces a white granular precipitate. (Berthier, *N. Ann. Chim. Phys.* 7, 82.)—A solution of bichloride of platinum in alcohol gradually loses its power of precipitating potash-salts, being

converted into the inflammable chloride of platinum discovered by Zeise. According to Gehlen (*A. Gehl.* 3, 571), the ethereal solution, when exposed to light, becomes pale yellow and deposits platinum.—The aqueous solution is not precipitated in the dark, either by excess of carbonate of soda or by lime; but on exposure to light, compounds of platinic oxide with soda or lime are deposited. (*vid. inf.*) For the other reactions, vid. *Platinic Salts* (pp. 283—285).

*Hydrated Bichloride of Platinum.*—The aqueous solution concentrated by evaporation solidifies, on cooling, in brown-red needles, radiating from the centre of the vessel; they contain 36·91 p. c. of platinum, and are therefore composed of $PtCl^2$,10Aq. (Mather, *Sill. Amer. J.* 27, 262.)

*Aqueous Bichloride of Platinum*, or *Hydrochlorate of Platinic Oxide.*—This is the ordinary solution of platinum. Bichloride of platinum dissolves in water with evolution of heat. The solution in the pure state is brownish yellow. The browner colour which it generally exhibits proceeds from iridium. A dark brown tint is also given to it by the presence of protochloride of platinum, *e.g.*, when the platinum-solution is heated, after evaporation, till it begins to give off chlorine, and the residue is redissolved in water. (Berzelius.)

D. *Chlorosulphide of Platinum?*—From a solution of platinum in aqua-regia, sulphuretted hydrogen throws down a mixture of sulphide and chloride of platinum, which detonates in particular parts when heated. (Berzelius, *Lehrb.*)

E. *Chloriodide of Platinum?*—When a solution of bichloride of platinum is mixed with excess of hydriodic acid and evaporated to dryness (hydrochloric acid then escaping) and the residue heated to 149°, (whereby the excess of hydriodic acid is driven off, together with chloride of iodine,) a mixture of bichloride and biniodide of platinum is left, in the form of a black powder. An analysis gave: 32·50 per cent. of platinum, 59·61 iodine, 7·03 chlorine (loss 0·86).—Between 205° and 315°, the mixture gives off brownish-yellow vapours of chloride of iodine and violet vapours of iodine, and leaves spongy platinum. It dissolves in aqueous potash, forming a red solution, from which it is precipitated unchanged on the addition of sulphuric acid. It is insoluble in water, slightly soluble in alcohol. (Mather, *Sill. Am. J.* 27, 257.)

F. *Nitric Oxide with Bichloride of Platinum?*—A solution of platinum in aqua-regia is evaporated, with frequent addition of aqua-regia, till half of the liquid crystallizes on cooling; the crystals are then collected on a filter, and pressed between bibulous paper.—Small orange-yellow crystals.—They give off no water at 100°. They deliquesce rapidly in the air. When water is poured upon them, a solution of bichloride of platinum is formed, and nitric oxide escapes with brisk effervescence. (Rogers & Boyé, *Phil. Mag. J.* 17, 397; also *J. pr. Chem.* 26, 150.)

| | Rogers & Boyé. |
|---|---|
| Pt | 41·26 |
| Cl | 43·89 |
| $NO^2$ | 4·89 |
| HO and loss | 9·96 |
| | 100·00 |

No formula can be deduced from this analysis.

The author likewise obtained this compound by digesting spongy platinum with aqua-regia for several days, in a basin covered with glass and placed over the water-bath, and afterwards leaving it to cool. At the bottom of the brown mother-liquid there were found, together with undissolved spongy platinum, yellow granular crystals, which, when covered with water in a vessel containing air, evolved red fumes, but in a vessel filled with carbonic acid, gave off colourless nitric oxide.

## Platinum and Fluorine.

Bifluoride of Platinum, and Hydrofluate of Platinic Oxide.—A solution of fluoride of potassium is dropped into an aqueous solution of bichloride of platinum not containing excess of acid, as long as a precipitate of chloroplatinate of potassium continues to form. The liquid is then filtered and evaporated; the fluoride of platinum dissolved out by alcohol, which still leaves behind a small quantity of chloroplatinate of potassium; and the alcoholic liquid mixed with water, and again evaporated. If only a slight degree of heat be applied, there remains a non-crystalline, yellow, transparent mass, which redissolves completely in water; at 60°, on the other hand, the mass becomes dark brown, and when dissolved in water leaves a brown basic salt.—Bifluoride of platinum combines with the fluorides of the alkali-metals, forming fluorine-salts. (Berzelius.)

## Platinum and Nitrogen.

A. Nitrate of Platinous Oxide, or Platinous Nitrate.—Hydrated platinous oxide dissolves in dilute nitric acid, forming a greenish-brown solution, which appears almost black when evaporated to dryness; the solution, however, contains a large quantity of platinic oxide, which is gradually produced in greater abundance, the more the acid is in excess. (Berzelius.)

B. Nitrate of Platinic Oxide, or Platinic Nitrate.—1. By dissolving hydrated platinic oxide in nitric acid.—2. By decomposing platinic sulphate with an exactly equivalent quantity of nitrate of baryta, and filtering.—3. By adding nitre to aqueous bichloride of platinum, as long as chloroplatinate of potassium is deposited:

$$3PtCl^2 + 2(KO,NO^5) = 2(KCl,PtCl^2) + PtO^2,2NO^5.$$

According to this equation, $\frac{1}{3}$ of the platinum remains dissolved in the form of nitrate. The decanted dark brown liquid yields on evaporation a mass of the consistence of honey, which, after evaporation at a strong heat, dissolves but partially in water, leaving a basic salt. (Berzelius.)

C. Ammonio-protoxide of Platinum, or Platinite of Ammonia. —*a. With 2 At. Ammonia.*—$2NH^3,PtO,HO$.—After the discovery of ammonio-protochloride of platinum (p. 300) by Magnus, a series of salts was discovered by Gros, which may be supposed to contain the base, $2NH^3,PtClO$ (*Platinum-basis of Gros*); and two other series of salts by Reiset, the one containing the base, $2NH^3,PtO$ (*Reiset's first Platinum-basis*); and the second, $NH^3,PtO$ (*Reiset's second platinum-basis*). Other formulæ may likewise be given for these bases; thus Berzelius gives for Gros's base, $NH^2,PtCl + NH^4O$; and for Reiset's first

base, $NH^2Pt + NH^4O$. [For Gerhardt's theory of these compounds, see p. 313, et seq.]

This compound is obtained by precipitating the solution of the sulphate ($2NH^3, PtO, SO^3$) with the proper quantity of baryta-water, evaporating the filtrate out of contact of air, and finally in vacuo over oil of vitriol, till it solidifies in a mass consisting of white needles and becoming opaque when perfectly dry. The crystalline mass thus dried contains 1 At. water, and is composed of $2NH^3, PtO, HO$. According to Berzelius, it is $NH^3, PtO + NH^4O$. Its taste is very alkaline and caustic, like that of potash, and its solution absorbs carbonic acid greedily from the air, and decomposes starch-sugar just like a solution of potash. (Reiset.) From a solution of nitrate of silver, it throws down silver-oxide, just as potash does. (Peyrone.)—The crystalline mass fuses at 110°, gives off 1 At. ammonia and 1 At. water with strong intumescence, and leaves $NH^3, PtO$. (Reiset.) It deliquesces in the air, and its aqueous solution does not give off ammonia, even when boiled. (Reiset.) With 1 At. of the different oxygen acids, it forms a series of perfectly neutral salts, from which it is separated again in its original state, by stronger bases. The solutions of these salts deposit metallic platinum after long standing, but without the formation of an ammoniacal salt; it is therefore probable that similar salts exist, containing the bioxide instead of the protoxide of platinum. (Reiset.) Slightly soluble in alcohol. (Peyrone.)

*b. With 1 At. Ammonia.*—$NH^3, PtO$.—Remains in the form of a greyish mass when the compound *a* is heated above 110°.—When heated in a retort above 200°, it is quietly resolved into nitrogen gas, ammonia, water and platinum. Probably $Pt^3N$ is first produced, and is afterwards resolved into nitrogen gas and platinum:

$$3(NH^3, PtO) = Pt^3N + 3HO + 2NH^3.$$

But if it be heated to 200° at one point with access of air, it becomes red-hot, the glow spreading from that point, and makes a hissing noise. In this case, the spongy platinum induces the combination of the hydrogen in the ammonia with the oxygen of the air, just as it acts upon hydrogen gas mixed with air. This base is insoluble in water and ammonia, and combines with acids, forming detonating salts which are insoluble in water. (Reiset.)

D. Ammonio-binoxide of Platinum, or Platinate of Ammonia.—*a. Fulminating Platinum.*—1. Formed by decomposing chloroplatinate of ammonium with aqueous potash. The precipitate requires a higher temperature to explode it than fulminating gold or silver, and does not detonate so violently. (Proust, *N. Gehl.* 1, 348.)—According to Döbereiner (*Gilb.* 72, 194), the straw-coloured precipitate contains 3 At. platinic oxide with 1 At. ammonia, and detonates slightly when rapidly heated, but strongly when subjected to a gradual heat.

2. By dissolving platinum sal-ammoniac in a very large excess of aqueous potash, and precipitating the fulminating platinum from the filtrate by neutralizing with hydrochloric acid. It detonates slightly when suddenly heated, strongly when exposed to a gradual heat. (Fourcroy & Vauquelin, *N. Gehl.* 1, 348.)

3. By precipitating aqueous platinic sulphate with ammonia, boiling the precipitate with potash-ley, and then washing and drying.—Brown powder, permanent in the air.—Contains 73·75 per cent. of platinum combined with 8·75 of oxygen, 9·00 of ammonia and 8·50 of water.

Does not explode by friction, percussion, or the electric spark, but detonates violently when heated to 205°. It is converted by chlorine-water into sal-ammoniac and aqueous bichloride of platinum; yields when heated with nitric acid, the peculiar oxide of platinum described on p. 282; dissolves in sulphuric acid without evolution of gas, and forms a dark brown solution; and is not sensibly attacked by hydrochloric acid. (E. Davy, *Schw.* 19, 91.)

*b.* $NH^3,PtO^2+2Aq$.—Gerhardt's Platinamine = $NHpt^2+2Aq$. (p. 314).

E. Ammonio-carbonate of Platinous Oxide.—The compound $2NH^3,PtO$ dissolved in water, is converted, on exposure to the air, first into $2NH^3,PtO,CO^2,HO$, and afterwards into $2NH^3,PtO,2CO^2,HO$. (Reiset.) The former compound is likewise produced in the decomposition of $2NH^3,PtCl$ by aqueous monocarbonate of potash. (Peyrone.)

F. Sulphoplatinate of Ammonium.—Sulphide of platinum precipitated by sulphuretted hydrogen, dissolves in hydrosulphate of ammonia, forming a red-brown solution, from which it is precipitated by acids with the same colour. (Berzelius.)

G. Sulphite of Platinous Oxide and Ammonia.—$NH^4O,SO^2+PtO,SO^2$.—Falls down as a white, crystalline precipitate, when a solution of bichloride of platinum, decolorized by sulphurous acid gas, is neutralized with ammonia and mixed with absolute alcohol. The salt purified by washing with alcohol dissolves easily in water, forming a colourless liquid, which gives with nitrate of silver a peculiar precipitate, different from chloride of silver, and is not precipitated by potash. It likewise gives no precipitate with alkaline hydrosulphates; but on the subsequent addition of hydrochloric acid, a yellow precipitate is formed, which, when the mixture is heated, first turns brown, and afterwards black. (Liebig, *Pogg.* 17, 108, and *Ann. Pharm.* 23, 23; Böckmann, *Liebig, Traité de Chim. Org.* Paris, 1840, 102.)

When sulphurous acid gas is passed through an aqueous solution of bichloride of platinum, till the latter no longer gives a precipitate with sal-ammoniac, the liquid left to itself for a few days in a stoppered bottle, and ammonia afterwards added, at least three compounds are formed, consisting of sulphurous acid, platinous oxide, and ammonia: *a.* Nearly insoluble in water; hydrochloric acid converts it, with evolution of sulphurous acid, into a chlorine-compound consisting of shining lemon-yellow, or orange-yellow crystals.—*b.* More easily soluble; solidifies on cooling in transparent and colourless needles; behaves with hydrochloric acid like *a.*—*c.* Very easily soluble; does not crystallize on evaporation, but separates in the form of a white powder; when treated with hydrochloric acid, it yields a yellow powder, similar to the yellow body, $NH^3,PtCl$ (p. 302). (Peyrone.)

H. Ammonio-sulphate of Platinous Oxide.—*a. With 2 At. Ammonia.*—$2NH^3,PtO,SO^3$.—*a. Yellow.*—1. Reiset's soluble compound ($2NH^3,PtCl,HO$) is decomposed by sulphate of silver-oxide, and the filtrate evaporated to the crystallizing point. (Reiset.)—2. The same chlorine-compound is decomposed by moderately strong sulphuric acid, the action being attended with evolution of hydrochloric acid. (Peyrone.) Crystallizes with facility, and is neutral to vegetable colours. (Reiset.) Always forms yellow, transparent, square-based octohedrons. (Peyrone.)

*β. Colourless.*—Formed by decomposing Peyrone's transparent and colourless crystalline compound $2NH^3, PtCl$ (p. 300) with moderately strong sulphuric acid. Each drop of the acid added to the solution of the chlorine-compound throws down white pearly scales of an acid salt, which, however, when dissolved in warm water and subsequently cooled, yields crystals of the mono-acid salt, while the excess of sulphuric acid remains with the water. Transparent and colourless square-based octohedrons, which have no action on vegetable colours. Slightly soluble in cold water; dissolves in 50 or 60 parts of boiling water. Insoluble in alcohol of ordinary strength. The solution of the salt in dilute sulphuric acid yields scales of the acid salt when evaporated; but on further evaporation, it deposits blood-red needles, which are quickly transformed into the red scales; when the solution is still further evaporated, a black mass is formed, and on dissolving this mass in water, metallic platinum remains behind. (Peyrone.)

| | *Crystallized, dried at* 100°. | | | Peyrone. | | |
|---|---|---|---|---|---|---|
| | | | | *a.* Yellow. | | *β.* Colourless. |
| 2N | 28 | .... | 15·47 | | | |
| 6H | 6 | .... | 3·32 | ..... 3·76 | .... | 3·50 |
| Pt | 99 | .... | 54·69 | ..... 54·19 | .... | 54·38 |
| O | 8 | .... | 4·42 | | .... | |
| $SO^3$ | 40 | .... | 22·10 | ..... 22·12 | .... | 22·26 |
| $2NH^3, PtO, SO^3$ | 181 | .... | 100·00 | | | |

*b. With* 1 *At. Ammonia.*—$NH^3, PtO, SO^3 + HO$.—Formed by boiling the iodine-compound ($NH^3, PtI$) with aqueous silver-sulphite, the ebullition being continued for a long time, because the decomposition takes place but slowly. The salt reddens litmus strongly. The 1 At. water which it contains cannot be separated. By solution in ammonia, it is converted into the salt *a*, *a*, just considered. (Reiset.)

I. Ammonio-sulphate of Platinic Oxide.—*Basic.*—On neutralizing platinic sulphate with ammonia, and boiling for a few minutes, the liquid becomes colourless, and a pale brown, tasteless powder is precipitated, which is permanent in the air, detonates slightly when heated, is decomposed by a boiling solution of potash, and dissolves in hot hydrochloric or sulphuric acid, but not in water. (E. Davy.)

K. Ammonio-protiodide of Platinum.—*a. With* 2 *At. Ammonia.*—$2NH^3, PtI$. —Formed by decomposing the aqueous sulphate $H, a, a$ ($2NH^3, PtO, SO^3$), with iodide of barium, and evaporating the filtrate.—Cubes.—The aqueous solution, when boiled, gives off 1 At. ammonia, and deposits the following compound. (Reiset.)

*b. With* 1 *At. Ammonia.*—$NH^3, PtI$.—Precipitated on boiling the aqueous solution of the compound *a*. Yellow powder, which dissolves in ammonia, and is thereby reconverted into the compound *a*. (Reiset.)

L. Iodoplatinate of Ammonium.—The solution of biniodide of platinum in hydriodate of ammonia, obtained by digestion at a gentle heat, yields, on evaporation, small, metallic-looking, blackish, square tables, which are anhydrous and permanent in the air. When heated, they give off nitrogen, ammonia, iodine, and hydriodate of ammonia, and leave 23 per cent. of platinum. They dissolve sparingly in water, forming a red solution, but are insoluble in alcohol. (Lassaigne, *J. Chim.*

*méd.* 8, 715.) Kane (*Phil. Mag. J.* 2, 198), by mixing a solution of biniodide of platinum in aqueous hydriodic acid with ammonia, obtained a black precipitate, which in a few minutes became brown, and afterwards of a fine red colour; it was found to contain 144 pts. (1 At.) of hydriodate of ammonia and 1,425 pts. (5 At.) of sesqui-iodide of platinum.

| | *Crystallized.* | | Lassaigne. |
|---|---|---|---|
| $NH^4I$ | 144 | 17·02 | 17·01 |
| 2Pt | 198 | 23·40 | 23·00 |
| 4I | 504 | 59·58 | 59·99 |
| $NH^4I, 2PtI^2$ | 846 | 100·00 | 100·00 |

M. Ammonio-protobromide of Platinum.—$2NH^3, PtBr$.—Prepared by means of bromide of barium, just as the iodoplatinate is obtained with iodide of barium. It likewise crystallizes in cubes, but its aqueous solution is not decomposed by boiling. (Reiset.)

N. Ammonio-protochloride of Platinum.—*a.* With 2 *At. Ammonia.*—$2NH^3, PtCl$.—[Hydrochlorate of Diplatosamine = $N^2H^5Pt, HCl$.]—Protochloride of platinum is immersed in aqueous ammonia, and boiled with it, the liquid being frequently renewed, till the green compound of Magnus, which is formed at first, with evolution of heat, is dissolved,—after which the solution is evaporated to the crystallizing point. The green salt of Magnus may likewise be treated in a similar manner. (Reiset.) The solution obtained by boiling Magnus's green compound with ammonia is evaporated to dryness, the residue dissolved in cold water, the yellow solution gently evaporated, then cooled to the crystallizing point, and the product purified by recrystallization. Carbonate of ammonia cannot be used in the preparation; it is true that Magnus's green compound dissolves in it as readily as in caustic ammonia; but the crystals thus obtained are contaminated with a powder which effervesces with acids, and is very difficult to separate. (Peyrone.)—2. Sulphurous acid gas is passed through aqueous bichloride of platinum till the liquid is completely decolorized; sulphite of platinous oxide and soda precipitated from it by the addition of carbonate of soda; the precipitate dissolved in hydrochloric acid; and the resulting solution of chloride of sodium and protochloride of platinum saturated in the cold with a very large quantity of ammonia. The mixture of $2NH^3, PtCl$ and $NH^3, PtCl$, thereby precipitated, is dissolved in boiling hydrochloric acid. The filtrate, on cooling, deposits $NH^3, PtCl$, while $2NH^3, PtCl$ remains in solution. The latter separates out on evaporation, mixed however with sal-ammoniac; hence it is better to precipitate it from the solution by alcohol, wash with alcohol, dissolve in water, and leave the compound to separate from the solution by evaporation and cooling. Even when the crystals appear perfectly transparent and colourless, they may still be contaminated with $NH^3, PtCl$. To purify them from the latter, their solution in cold water is evaporated over the water-bath till needles begin to form, and increase considerably as the liquid cools; the mother-liquor is then poured off, and the needles pressed between bibulous paper, and dried at 100°. (Peyrone.)

Prepared by (1) it forms beautiful needles. (Reiset.) Transparent, straw-yellow, four-sided needles. (Peyrone.)—By (2): transparent, colourless, brittle, four-sided needles, without action on vegetable colours, and having a pure saline taste. (Peyrone.)

| | *Crystallized, dried at* 100°. | | | Peyrone. (1) | | (2) |
|---|---|---|---|---|---|---|
| 2N | 28·0 | .... | 16·63 | ..... | | |
| 6H | 6·0 | .... | 3·56 | ..... | 3·92 | .... 3·81 |
| Pt | 99·0 | .... | 58·79 | ..... | 58·29 | .... 58·30 |
| Cl | 35·4 | .... | 21·02 | ..... | 20·99 | .... 20·86 |
| | 168·4 | .... | 100·00 | | | |

Reiset (*Compt. rend.* 10, 870) assigns the same composition to this substance; but more recently (*Compt. rend.* 18, 1103) he supposes it to contain 1 At. water, making the formula, $2NH^3,PtCl + HO$.

Peyrone supposes that the compound prepared by his process (2) is different from that of Reiset,—notwithstanding the similarity of constitution and general resemblance in other respects,—inasmuch as (1) is yellow, and forms yellow salts with oxygen-acids (of which colour, however, Reiset says nothing), whereas (2) is colourless, and forms colourless salts; and moreover (1) is somewhat less soluble in water and alcohol.

When the crystallized compound obtained by (1) is heated in a tube, it gives off 1 At. ammonia, at about 250°, and leaves the yellow compound $NH^3,PtCl$; at a higher temperature, it emits dense fumes of sal-ammoniac, and ultimately of hydrochloric acid, while metallic platinum remains behind. (Reiset.) The evolution of ammonia from the compound (2) begins at 220°, and becomes more energetic at 240°. If the heat be discontinued, when the evolution of ammonia ceases, and the residue be dissolved in boiling water, the solution yields, on cooling, yellow, translucent crystals of $NH^3,PtCl$. (Peyrone.) The compound (1) heated with caustic potash gives off no ammonia till heated to the boiling point. (Reiset.) (2) is decomposed by carbonate of potash, slowly in the cold, instantly at temperatures between 40° and 50°, yielding chloride of potassium and ammonio-carbonate of platinous oxide. (Peyrone.)

$$2NH^3,PtCl + KO,CO^2 = 2NH^3,PtO,CO^2 + KCl.$$

Potassium-amalgam forms with the pulverized crystals (2), chloride of potassium, and a black powder containing mercury, platinum, and a large quantity of ammonia. (Peyrone.)

$$2NH^3,PtCl + Hg^xK = 2NH^5,PtHg^x + KCl.$$

The crystals (2) evaporated to dryness with excess of hydrochloric acid, leave a mixture of sal-ammoniac and yellow $NH^3,PtCl$. (Peyrone.)—The crystals (1) dissolve in gently heated nitric acid, with evolution of nitrous gas, forming a liquid, from which the nitric acid salt of Gros ($2NH^3,PtClO,NO^5$) separates out. (Reiset.) According to Peyrone, on the other hand, the crystals (2), when treated with sulphuric, nitric, or oxalic acid, give off the whole of their chlorine in the form of hydrochloric acid, and are converted into salts whose base consists of $2NH^3,PtO$; *e. g.*:

$$2NH^3,PtCl + HO,SO^3 = 2NH^3,PtO,SO^3 + HCl.$$

Chlorine gas passed through the solution, converts the crystals (1) into the chlorine-compound of Gros ($2NH^3,PtCl^2$). (Reiset.) Silver-salts are decomposed by contact with it, yielding chloride of silver and salts having $2NH^3,PtO$ for their base. (Reiset.)—The aqueous solution of (2) is immediately converted, by contact with protochloride of platinum, into the green compound of Magnus. (Peyrone.)

$$2NH^3,PtCl + PtCl = 2(NH^3,PtCl).$$

The crystals (1) dissolve readily in water and in aqueous ammonia, and are precipitated from the solutions by alcohol. (Reiset.) The crystals (2) are slightly soluble in alcohol of ordinary strength, insoluble in absolute alcohol. (Peyrone.)—The solution of the compound (1) mixed with less than the equivalent quantity of aqueous bichloride of platinum, yields a copious olive-green precipitate = $2(2NH^3,PtCl) + PtCl^2$. — If, on the contrary, the solution of bichloride of platinum is in excess, a pale-red crystalline powder is precipitated, = $2NH^3,PtCl + PtCl^2$. (Reiset.)

*b. With* 1 *At. Ammonia.* — $NH^3, PtCl$. — [Hydrochlorate of Platosamine = $NH^2, Pt, HCl$.] — *a. Yellow.*—1. This compound is obtained by proceeding as in the second mode of preparing the preceding compound *a* (p. 300). From the solution in boiling hydrochloric acid of the precipitate obtained by ammonia, the compound *b* separates on cooling, first as a yellow powder, afterwards in small yellow crystals, while the compound *a* remains in solution. The precipitate, after washing with water, is purified by dissolving it twice in hot hydrochloric acid. (Peyrone.)—2. Bichloride of platinum is heated to 250°, to convert it into protochloride; the latter dissolved in hydrochloric acid; the solution neutralized with carbonate of ammonia, and the mixture heated to the boiling-point, with further addition of ammonia equal in quantity to that already introduced, whereupon the garnet colour of the liquid gradually changes to straw-yellow, and a dingy green substance is deposited after a while. If the liquid be filtered just at this moment, the filtrate, on further cooling, will deposit the yellow crystalline substance; the remaining liquid must then be quickly decanted, otherwise the yellow substance will redissolve in the carbonate of ammonia therein contained. To free the yellow body from two dingy green substances with which it is mixed, it is digested in boiling water, and filtered; one green substance is then left on the filter, while the other remains dissolved in the water, from which the pure yellow substance then separates out. (Peyrone.)—3. The pulverized compound *a* ($2NH^3,PtCl$) is heated in a basin on the sand-bath to a temperature between 220° and 270°, constantly stirred, as long as ammonia continues to go off, and removed from the fire as soon as fumes of sal-ammoniac make their appearance. (Peyrone, Reiset.)—4. The compound *a* is mixed with a large excess of hydrochloric acid and evaporated to dryness, the resulting sal-ammoniac being dissolved out by water. (Peyrone.)—5. The solution of $NH^3,PtO,SO^3$, or of $NH^3,PtO,NO^5$, mixed with hydrochloric acid or a dissolved metallic chloride, deposits a crystalline powder in a few seconds. (Reiset.)—6. When Magnus's green compound is boiled for some time with a concentrated solution of sulphate or nitrate of ammonia, it dissolves, and separates out again, as the solution cools, not in its original state, but converted into yellow scales. (Reiset.)—¶ 7. The yellow modification may also be obtained in quantity by adding solution of potash in small successive portions to a solution of protochloride of platinum neutralized with carbonate of ammonia, and kept at a temperature of 13°. (Peyrone.) ¶

Yellow powder (when prepared by (2) it has a tinge of orange-yellow), or small yellow crystals. (Peyrone.)—Beautiful yellow crystalline powder, or crystalline scales. (Reiset.)

| | | | | | Peyrone. |
|---|---|---|---|---|---|
| N | 14·0 | .... | 9·25 | ..... | 9·00 |
| 3H | 3·0 | .... | 1·98 | ..... | 2·18 |
| Pt | 99·0 | .... | 65·39 | ..... | 65·06 |
| Cl | 35·4 | .... | 23·38 | ..... | 23·32 |
| $NH^3,PtCl$ | 151·4 | .... | 100·00 | ..... | 99·56 |

Decomposes at about 270°, with evolution of sal-ammoniac vapours and hydrochloric acid, and finally leaves metallic platinum:

$$3(NH^3,PtCl) = 3Pt + 2(NH^4Cl) + HCl + N.$$

Cold oil of vitriol has no action on the yellow body; hot oil of vitriol liberates hydrochloric and sulphurous acid, and leaves a yellowish-brown substance which is decomposed by boiling water. Nitric acid converts the yellow body, without separation of platinum, into the two following substances: (*a*). Small, transparent, lemon-yellow, regular octohedrons, containing 51·37 per cent. of platinum, easily soluble in water, somewhat less soluble in alcohol.—(*β*). Syrupy, non-crystallizing, easily soluble in water and alcohol; forms crystallizable compounds with sesquichloride of iron, protochloride of mercury, and bichloride of platinum.—The yellow body is decomposed by silver-salts, with formation of chloride of silver.—It dissolves completely in carbonate of ammonia, forming the compound $2NH^3,PtCl$, which, however, when thus produced, differs greatly in its physical properties from Reiset's compound. (Peyrone.)—It dissolves in aqueous ammonia, forming the crystalline compound $2NH^3,PtCl$. (Reiset.) It dissolves in aqueous carbonate of potash, and sparingly, but without alteration, in water, hydrochloric acid, and dilute sulphuric acid. (Peyrone.) Slightly soluble in boiling water. (Reiset.)

¶ *β. Red Modification.*—1. When carbonate of ammonia, instead of being at once added in excess to a neutral solution of protochloride of platinum heated to 100° (as in *a*, 2), was added drop by drop to a solution of that salt in a state of rapid ebullition, no change of colour took place, a sign that the yellow salt was not produced; but the solution, when left to cool slowly, deposited small, very beautiful, garnet-coloured crystals, in the form of six-sided tables. The crystals were insoluble in cold water, and were decomposed by boiling water, the whole of the platinum being separated. When the crystals were treated with nitric acid, products were formed, probably analogous to those which are produced, under similar circumstances, from Magnus's green salt. This salt is precisely similar in composition to the preceding. It was, however, only formed once, all endeavours to reproduce it being fruitless.—2. On adding a small quantity of carbonate of ammonia to a boiling, very dilute, and neutral solution of protochloride of platinum, a very small quantity of minute shining scales are formed, having a reddish colour, similar to that produced by passing carbonic acid gas through tincture of litmus. These scales are distinguished from the preceding substance by being soluble in cold, and still more in boiling water; moreover, they are not decomposed by the latter. They are extremely light, the slightest motion in the air being sufficient to carry them up.—With nitric acid, this substance behaves like the preceding; also with ammonia, excepting that its conversion into Magnus's salt, by the action of the latter, takes place only at a boiling heat. Its composition is exactly similar. (Peyrone.)—3. A quantity of the mother-liquid obtained in the preparation of the yellow salt, was mixed with ammonia, and boiled, in order to convert any of the yellow salt that might be contained in the solution into the compound $2NH^3,PtCl$. After the excess of ammonia had been driven off, a solution of protochloride of platinum was added by small portions at a time. No formation of the green salt took place, and the solution retained its original colour; but as the liquid cooled, small octohedrons, apparently with square bases, and of a bright-red, or orange-red colour, separated from it. These crystals are very slightly soluble in cold water, and dissolve in about 50 times their weight of boiling water. When dissolved and

recrystallized, they undergo slight modifications of colour and grouping, arranging themselves in fern-like tufts, and acquiring by repeated crystallization first an orange-red, then an amber-yellow, and finally a yellowish green or olive-green colour. Ammonia at a boiling heat dissolves them readily, without formation of Magnus's green salt. The resulting solution is transparent and perfectly colourless; when cautiously evaporated, it deposits small, colourless, prismatic needles, together with a yellow amorphous substance. The products formed by the action of nitric acid on this compound appear to be the same as those which are obtained in a similar manner from the yellow salt prepared by the direct process. (Peyrone.)—4. The mother-liquid of one of the preceding preparations yielded a substance much more soluble in the water than the last, but resembling it in all other respects. The four compounds just described all agree in composition with the yellow salt, *a*, as appears from the following analyses:

| | | | | | Peyrone. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | (1) | | (2) | | (3) | | | (4) |
| N | 14·0 | .... | 9·25 | .... | 9·40 | .... | | .... | 9·74 | .... | | |
| 3H | 3·0 | .... | 1·98 | .... | 2·13 | .... | | .... | 2·05 | .... | | |
| Pt | 99·0 | .... | 65·39 | .... | 64·99 | .... | 65·25 | .... | 64·96 | .... | | 64·90 |
| Cl | 35·4 | .... | 23·38 | .... | 23·48 | .... | 23·46 | .... | 23 25 | .... | | 23·38 |
| $NH^3,PtCl$ | 151·4 | .... | 100·00 | .... | 100·00 | .... | | .... | 100·00 | | | |

(Peyrone, *Ann. Pharm.* 55, 207.) ¶

*γ. Green Modification.—Magnus's Green Compound.*—May likewise be regarded as $2NH^3,PtCl + PtCl$, inasmuch as it is immediately formed on mixing the aqueous solution of $2NH^3,PtCl$ with PtCl. (Peyrone.)—[Chloroplatinate of Diplatosamine = $PtCl^2H,N^2H^5Pt$].—1. The solution of the brown protochloride of platinum in hydrochloric acid, supersaturated with ammonia, deposits the green compound after a while. (Magnus, *Pogg.* 14, 242.)—2. Sulphurous acid gas is passed through a gently-heated aqueous solution of bichloride of platinum, till the solution no longer gives a precipitate with sal-ammoniac. If the stream of gas be too long continued, the liquid becomes decolorized, and is then no longer adapted for the preparation of the green compound. On heating the liquid after the proper quantity of sulphurous acid has been passed through it, and then supersaturating with ammonia, it becomes turbid, and deposits green, needle-shaped crystals, which must be washed with water. (J. Gros, *Ann. Pharm.* 27, 241; also *Ann. Chim. Phys.* 69, 204.)—3. The mother-liquid from which the greater part of the colourless chlorine-compound, $2NH^3,PtCl$ (p. 300, preparation 2) has separated, is mixed with recently-prepared protochloride of platinum (obtained from the bichloride by the action of sulphurous acid), and the needles which immediately separate are washed with water. (Peyrone.)

Green, crystalline (Magnus). Needles (Peyrone).

| | | | | | Magnus. | | Gros. |
|---|---|---|---|---|---|---|---|
| 2N | 28·0 | .... | 9·25 | } | 10·89 | .... | { |
| 6H | 6·0 | .... | 1·98 | } | | | { 2·02 |
| 2Pt | 198·0 | .... | 65·39 | .... | 65·65 | .... | 65·36 |
| 2Cl | 70·8 | .... | 23·38 | .... | 23·46 | .... | 23·05 |
| $2NH^3,PtCl + PtCl$ | 302·8 | .... | 100·00 | .... | 100·00 | | |

This compound, when heated to redness, leaves a residue of platinum, part of which, however, is carried away with the sal-ammoniac vapours, unless carbonate of soda be added to it. (Gros.) Does not evolve

ammonia when boiled with potash-ley, or give up ammonia to boiling hydrochloric or sulphuric acid. (Gros.)—Does not dissolve or decompose in water, hydrochloric acid, or alcohol. (Magnus.)—Dissolves when boiled for some time in aqueous ammonia, and the solution, as it cools, deposits needles of $2NH^3,PtCl$. (Reiset.)

¶ *Compounds obtained by the action of Sulphite of Ammonia on the Green Salt of Magnus and its Yellow Modification.*—The green salt of Magnus heated to the boiling point with an equal quantity of sulphite of ammonia, yields a white powder, perfectly insoluble in alcohol and in cold water, and very sparingly soluble in boiling water. Its composition is $PtN^2H^7O^2,2SO^2 + 2(PtNH^3O,SO^2)$.—When the sulphite of ammonia is in excess and the liquid is boiled for a long time, a solution is formed from which alcohol throws down oily drops, uniting together into a glutinous mass, of variable composition, which solidifies after being left for some time in contact with alcohol. The alcohol used for the precipitation deposits, if left to stand quietly, small white flakes of a body having the composition: $PtN^2H^7O^2,2SO^2 + NH^4O,SO^2$.—The modification of Magnus's compound which crystallizes in orange-yellow octohedrons (p. ) is more easily attacked by sulphite of ammonia than the green compound, and forms with it two white bodies, viz., a white pulverulent body, insoluble in water, and having the composition assigned to the first of the salts formed from Magnus's green compound; and another compound soluble in water in all proportions, precipitated by alcohol in oily drops, and afterwards solidifying; its composition is: $PtN^2H^7O^2, 2SO^2 + 2(NH^4O,SO^2)$.—The yellow modification obtained by the direct method requires 33 parts of boiling water to dissolve it. An excess of it boiled for a sufficient time with sulphite of ammonia, yields small white unctuous needles, whose composition is expressed by the formula: $PtN^2H^7O^2,2SO^2 + 2(NH^4O,SO^2) + PtNH^3Cl + HO$.—The yellow modification prepared by reduction requires 140 parts of boiling water to dissolve it; an excess of it boiled for a sufficient time with sulphite of ammonia, forms a body which crystallizes in thin transparent rhombic tables, and is composed of: $PtN^2H^7O^2,2SO^2 + PtNH^3Cl + 2HO$. With an excess of sulphite of ammonia, on the contrary, the product obtained is Böckmann's salt: $PtN^2H^7O^2,2SO^2$. — The chlorine-compounds obtained by treating these isomeric bodies with ammonia, yield, under the influence of sulphite of ammonia, at ordinary temperatures, a substance crystallizing in prismatic four-sided needles, transparent, scarcely soluble in cold water, but soluble in 190 times its weight of boiling water; at ordinary temperatures, it is composed according to the formula: $PtNH^3O,SO^2 + PtN^2H^6O,SO^2 + 2HO$. These same chlorine-compounds, when boiled, give off ammonia, and are converted into Böckmann's salt. (Peyrone, *Ann. Pharm.* 61, 178.) ¶

O. Ammonio-bichloride of Platinum.—*a.* $2NH^3,PtCl^2$.—[Bi-hydrochlorate of Diplatinamine, $N^2H^4pt^2,2HCl$ (p. 316).]—*a.* Anhydrous.—1. Formed by heating the nitrate, $2NH^3,PtClO,NO^5$ (p. 311), in the dry state with excess of strong hydrochloric acid, and evaporating to dryness, whereupon chlorine and hyponitric acid are evolved.—2. By mixing the aqueous solution of the same nitrate with hydrochloric acid or the chloride of an alkali-metal, which immediately precipitates the compound in the form of a white, heavy, sandy powder.—¶ 3. By passing chlorine into a boiling and somewhat concentrated solution of the compound $2NH^3,PtCl$. (Raewsky.)—4. By boiling the compound $NH^3,PtCl^2$ (C. *p.* 314) with ammonia, and expelling the excess of ammonia by evaporation; the salt

is then deposited in the form of a powder consisting of octohedral crystals. (Gerhardt.)—5. By adding hydrochloric acid to a solution of the nitrate, $2NH^3,PtO,NO^5$. (Gerhardt.)—6. By adding hydrochloric acid to Raewsky's nitrate (p. 312). (Gerhardt.) ¶

| | | | Gros. | Raewsky (3). | | Gerhardt. | |
|---|---|---|---|---|---|---|---|
| 2N | 28·0 | 13·74 | 13·74 | | | | |
| 6H | 6·0 | 2·94 | 2·99 | 3·10 | 3·00 | 3·06 | 3·18 |
| Pt | 99 0 | 48·58 | 47·44 | 48·13 | 48·25 | 48·50 | 48·33 |
| 2Cl | 70 8 | 34·74 | 33·75 | 33·48 | 34·00 | | |
| | 203·8 | 97·92 | 100·00 | | | | |

Gives off ammonia when fused with hydrate of potash, and leaves platinum together with chloride of potassium. When heated with excess of nitric acid, it is reconverted, with evolution of chlorine and hyponitric acid, into the nitrate ($2NH^3,PtClO,NO^5$). Nitrate of silver added in excess to the aqueous solution, immediately throws down part of the chlorine in the form of chloride of silver; but continued boiling is required to precipitate the whole. (Gros.)

¶ *Hydrated.*—$2NH^3,PtCl+HO$.—Formed by passing dry chlorine gas into a cold solution of the compound $2NH^3,PtCl$.—Yellowish salt, which, after drying at 120°, gives off water when heated in a tube. (Raewsky.)

| | *Dried at* 120°. | | Raewsky. | |
|---|---|---|---|---|
| 2N | 28·0 | 13·17 | 14·07 | 13·96 |
| 7H | 7·0 | 3·30 | 3·50 | 3·34 |
| Pt | 99·0 | 46·48 | 46·39 | 45·82 |
| 2Cl | 70·8 | 33·28 | 32·55 | 33·00 |
| O | 8·0 | 3·77 | 3·49 | 3·88 |
| | 212·8 | 100·00 | 100·00 | 100·00 |

*b.* $NH^3,PtCl^2$ = Bi-hydrochlorate of Platinamine, $NHpt^2,2HCl$ (p. 314). ¶

*c.* Platinum sal-ammoniac digested with aqueous ammonia yields a pale greenish-yellow powder. As a small quantity of nitrogen is evolved in this action, the compound is probably mixed with a small quantity of ammonio-protochloride of platinum (Magnus's green compound). (Berzelius, *Lehrb.*; comp. Fischer's experiments, pp. 307, 308; also Laurent and Gerhardt's experiments, p. 316.)

¶ P. Ammonio-chlorobromide of Platinum. — $2NH^3,PtClBr$. — When bromine is gradually added to a boiling and tolerably concentrated solution of the compound $2NH^3,PtCl$ (either Reiset's yellow, or Peyrone's white modification), a crystalline precipitate is immediately formed; and on subsequently adding bromine in excess, continuing the ebullition till the excess is driven off, and then leaving the solution at rest, crystals are formed having the composition above given; they are separated from the liquid by decantation, and washed with cold water.—Orange-yellow salt, nearly insoluble in cold water; gives with silver-solution, a precipitate of chloride and bromide of silver.

| | | *Crystallized.* | | Raewsky. *a.* | | *b.* | |
|---|---|---|---|---|---|---|---|
| 2N | 28·0 | 11·35 | | 11·36 | 11·36 | 10·96 | 10·80 |
| 6H | 6·0 | 2·43 | | 2·40 | 2·42 | 2·40 | 2·43 |
| Pt | 99·0 | 40·11 | | 39·77 | 40·00 | 40·00 | 40·28 |
| Cl | 35·4 | 14·34 | | 14·00 | 14·26 | 14·28 | 14·20 |
| Br | 78·4 | 31·77 | | 32·47 | 31·96 | 32·36 | 32·29 |
| $2NH^3,PtClBr$ | 246·8 | 100·00 | | 100·00 | 100·00 | 100·00 | 100·00 |

Q. Chloroplatinite of Ammonium.—*a.* Formed by mixing the purple-red solution of protochloride of platinum in concentrated hydrochloric acid with sal-ammoniac, and evaporating to dryness.—Purple-red, four-sided prisms, which turn brown after a while (from the action of light?) and become covered with a metallic film; they are easily soluble in water, and the solution is not precipitated by cold soda, but yields a black precipitate with hot soda, ammonia being at the same time evolved. (Vauquelin.)—Obtained in the same manner by Magnus, who used the hydrochloric acid solution of the brown protochloride of platinum.

*b.* Aqueous bichloride of platinum mixed with excess of sulphite of ammonia, gives at first the yellow precipitate of platinum sal-ammoniac; but on the application of heat, this precipitate dissolves, the liquid becomes decolorized, and after sufficient evaporation, deposits white crystalline grains, sparingly soluble in cold water, more readily in hot water; they probably consist of a compound of protochloride of platinum with sal-ammoniac. (Berthier, *N. Ann. Chim. Phys.* 7, 82.)

¶ *c.* When a solution of protochloride of platinum in hydrochloric acid is saturated with carbonate of ammonia, and the whole evaporated to dryness in the water-bath, a reddish residue is obtained, consisting of chloroplatinite of ammonium mixed with sal-ammoniac, which latter salt may be completely removed by repeated washing with alcohol. The washed residue must then be placed on fine filtering paper, and exposed to the air, till all traces of alcohol are removed; for the presence of alcohol produces some peculiar change in the compound, which interferes with its crystallization. It is then dissolved in boiling water, the solution filtered into a vessel previously heated, and then left to stand in a quiet place,—whereupon, if the cooling does not take place too quickly, very beautiful, four-sided prisms are obtained, sometimes more than a decimetre in length, and either acuminated at the ends or obliquely truncated; they are perfectly transparent, and of a fine garnet colour.

| | *Dried at* 100°. | | | Peyrone. |
|---|---|---|---|---|
| Pt | 99·0 | .... | 52·6 | 52 3 |
| 4H | 4·0 | .... | 2·1 | 2·2 |
| N | 14·0 | .... | 7·5 | 8·1 |
| 2Cl | 70·8 | .... | 37·8 | 37·4 |
| $NH^4Cl,PtCl$ | 187·8 | .... | 100·0 | 100·0 |

(Peyrone, *Ann. Pharm.* 55, 205.) ¶

R. Chloroplatinate of Ammonium.—*Platinum Sal-ammoniac.*—Precipitated in the form of a lemon-yellow, crystalline powder, on adding an ammoniacal salt to an aqueous solution of bichloride of platinum. A reddish yellow tint indicates the presence of chloriridiate of ammonium. This impurity may be nearly but not quite removed by repeated boiling with nitric acid; if the liquid be poured off hot, the chloriridiate of ammonium separates out from it on cooling, and the remaining liquid may be again boiled with the platinum residue. (Berzelius.)

Chloroplatinate of ammonium, when precipitated, forms a lemon-yellow, crystalline powder; when crystallised from its aqueous solution, it forms regular octohedrons of an orange-yellow colour.

| | *Crystallized.* | | | Vauquelin. |
|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 7·61 | |
| HCl | 36·4 | .... | 16·31 | |
| Pt | 99·0 | .... | 44·36 | 42·5 |
| 2Cl | 70·8 | .... | 31·72 | |
| $NH^4Cl,PtCl^2$ | 223·2 | .... | 100·00 | |

When heated to redness, it gives off, without fusion, nitrogen gas, hydrochloric acid, and sal-ammoniac, and leaves spongy platinum:

$$3(NH^4Cl,PtCl^2) = 3Pt + NH^4Cl + 8HCl + 2N.$$

On carefully heating it, not quite to redness, there remains a greyish green powder, which is neither dissolved nor decomposed by water, caustic potash, or acids, and is probably a compound of protochloride of platinum with sal-ammoniac. (Berzelius.) Chlorine gas passed through water in which chloroplatinate of ammonium is diffused, decomposes it with evolution of nitrogen (and formation of chloride of nitrogen), the products of the decomposition being an aqueous solution of bichloride of platinum and free hydrochloric acid:

$$NH^4Cl,PtCl^2 + 3Cl = PtCl^2 + 4HCl + N.$$

Chloroplatinate of ammonium is decomposed by heated oil of vitriol. It dissolves in a solution of protochloride of tin in hydrochloric acid, imparting a dark brown colour to the liquid. (Fischer.) It dissolves in 150 parts of cold water and in 80 parts of boiling water; 1 part of it imparts a yellowish colour, even to 20,000 parts of water. It is insoluble in cold hydrochloric acid, and separates out on cooling from its solution in hot hydrochloric, sulphuric, or nitric acid. (Fischer, *Kastn. Arch.* 14, 156.) A concentrated solution of sal-ammoniac precipitates chloroplatinate of ammonium almost completely from its aqueous solution. (Böttger.) Chloroplatinate of ammonium is insoluble in alcohol.

Chloroplatinate of ammonium is very slightly soluble in cold aqueous ammonia, but dissolves very abundantly and completely in a boiling solution of ammonia—provided it does not contain any foreign metals—forming a colourless or pale yellow liquid, which may be preserved in close vessels without alteration. (The aqueous solution of chloroplatinate of ammonium is likewise gradually decolorized by ammonia in the cold.) The ammoniacal solution, when exposed to the air, quickly becomes turbid, from loss of ammonia, and yields a greyish white precipitate, together with a white saline film consisting of the salt *a*, to be considered further on. If the solution be evaporated at a strong heat, it usually deposits chloroplatinate of ammonium; but by evaporation to dryness at a more gentle heat, it becomes pale yellow and acid, and finally deposits the greyish white powder of (*a*). The same compound is precipitated on gently adding ammonia to the liquid when it has become acid by gentle evaporation. It is also precipitated from the unevaporated solution, as a white gummy mass, by concentrated phosphoric, sulphuric, and nitric acid, and after a while also by hydrochloric acid; moreover, by alkaline carbonates, phosphates, sulphates, and oxalates; by green vitriol, in which case, however, hydrated ferrous oxide falls down with it, and must be dissolved out by hydrochloric acid, not in excess; very abundantly by alcohol; but not by alkaline hydrochlorates, nitrates, or acetates. An excess of most of these precipitants does no harm, inasmuch as they do not dissolve the compound (*a*); only phosphoric acid and phosphate of soda, and in a lower degree also, the alkaline carbonates, redissolve a small quantity of it. The precipitate produced by alkaline phosphates is not gummy, but curdy. If the ammoniacal solution has lost its excess of ammonia by long exposure to the air—in which case a small quantity of (*a*) separates out—the above-mentioned salts still throw down from it the white precipitate (*a*); but acids then separate the salt (*b*) in the form of a yellow or yellowish-red, gummy precipitate. This salt (*b*) is likewise precipitated in a few hours from the aqueous solution of

chloroplatinate of ammonium on the addition of phosphate or sulphate of soda. In all these precipitations, however, a large quantity of platinum remains dissolved.

Salt (*a*) is best prepared by precipitating the ammoniacal solution with phosphate of soda. White, gummy or curdy; deposited in indistinct laminæ, when the ammoniacal solution of chloroplatinate of ammonium is evaporated. Scarcely soluble in water, even at a boiling heat, or in dilute sulphuric acid, or in ammonia, (hence it does not exist ready formed in the ammoniacal solution of platinum sal-ammoniac). Dissolves in hot nitric acid, and separates again unchanged as the liquid cools. Dissolves in hot hydrochloric acid, and the solution, on cooling, deposits the yellow salt (*b*), which, however, disappears again on the addition of more water. Dissolves but sparingly in acid hydrochlorate of stannous oxide, imparting a pale yellow colour to the solution.

Salt (*b*). Most conveniently obtained by precipitating the ammoniacal solution of platinum sal-ammoniac with green vitriol, and treating the precipitate with excess of hydrochloric acid. Varies in colour from lemon-yellow to orange yellow, according to the concentration of the liquid from which the precipitate has been obtained. Gummy or fibrous. Fuses when heated, giving off sal-ammoniac without any free ammonia, and leaves platinum. Decomposed by hot oil of vitriol. In cold water it is less soluble than platinum sal-ammoniac; but in hot water it dissolves abundantly, forming a turbid, pale yellow liquid, from which it separates for the most part on cooling. Dissolves much more easily in acidulated water. In hot hydrochloric acid it dissolves more abundantly than (*a*), forming a yellowish solution, from which it separates on cooling, but redissolves on the addition of water. From its solution in hot dilute sulphuric acid, it likewise separates, on cooling, in the form of a yellow powder; but from solution in hot nitric acid, it separates in the form of (*a*). Acid hydrochlorate of stannous oxide dissolves it in small quantity, forming a deep yellow solution. (Fischer, *Kastn. Arch.* 14, 150.)

¶ S. *Raewsky's Carbonate.*—$4NH^3,Pt^2ClO^5,2CO^2$.—Formed by decomposing the corresponding nitrate (p. 312) with carbonate of ammonia. If concentrated solutions be used, a white granular precipitate is obtained; from dilute solutions, it separates, after a while, in pearly scales, which, however, are converted by drying into a white granular powder. (For the analysis and Gerhardt's formula, see page 317.) ¶

T. Ammonio-phosphate of Oxychloride of Platinum.—The nitrate ($2NH^3,PtClO,NO^5$), mixed with an aqueous alkaline phosphate, yields, after a while, small shining transparent crystals, much less soluble than the nitrate. (Gros.)

¶ U. *Raewsky's Phosphate.*—$4NH^3,Pt^2ClO^5,PO^5,HO$.—When a warm concentrated solution of the nitrate (p. 312) is mixed with terbasic phosphate of soda, a crystalline precipitate is immediately formed; from cold dilute solutions, the salt crystallizes, after a longer time, in small, white, strongly lustrous needles, arranged in radiated groups. It is nearly insoluble in cold water, and but slightly soluble in hot water. The basic water, amounting to 2·1 per cent., is given off at 150°. (For the analysis and Gerhardt's formula, *vid.* p. 318.) ¶

V. Ammonio-sulphate of Oxychloride of Platinum.—[Bichlor-

hydro-sulphate of Diplatinamine: $N^2H^4pt^2,SO^4H^2 + N^2H^4pt^2,2ClH$.]—1. The nitrate, $2NH^3,PtClO,NO^5$, and likewise the chlorine-compound $2NH^3,PtCl^2$, dissolve in warm dilute sulphuric acid, with evolution of hydrochloric or nitric acid, and subsequently yield crystals of the sulphate on cooling.—2. A warm concentrated aqueous mixture of one of these salts with sulphate of soda, solidifies, on cooling, in a viscid mass made up of needles. —Delicate transparent needles, which, when heated in contact with air, effloresce from loss of water.—Sparingly soluble in cold water, dissolves with tolerable facility in hot water, and separates from the solution unchanged. The hot solution, mixed with excess of nitric or hydrochloric acid, deposits the nitrate or chlorine-compound on cooling, the sulphuric acid remaining in the liquid. The aqueous solution gives no precipitate with baryta-salts, till nitric or hydrochloric acid is added to it. (Gros.)

| | *Dehydrated.* | | Gros. |
|---|---|---|---|
| 2N | 28·0 | 12·94 | 12·89 |
| 6H | 6·0 | 2·78 | 2·84 |
| Pt | 99·0 | 45·75 | 45·06 |
| Cl | 35·4 | 16·36 | 16·40 |
| O | 8·0 | 3·69 | 4·05 |
| $SO^3$ | 40·0 | 18·48 | 18·76 |
| $2NH^3,PtClO,SO^3$ | 216·4 | 100·00 | 100·00 |

¶ W. *Raewsky's Chlorine-compound.*—$2NH^3,PtClO,Cl$?—Hydrochloric acid added to a solution of the nitrate $4NH^3,Pt^2ClO^5,2NO^5$, produces a white granular precipitate, soluble in water.

| | *Dried at* 120°. | | Raewsky. | | | | Gerhardt. | |
|---|---|---|---|---|---|---|---|---|
| 2N | 28·0 | 13·23 | 13·40 | 13·50 | | | | |
| 6H | 6·0 | 2·83 | 2·66 | 2·70 | 3·06 | 3·18 | | |
| Pt | 99·0 | 46·74 | 47·30 | 47·10 | 48·50 | 48·43 | | |
| 2Cl | 70·8 | 33·43 | 31·30 | 32·00 | | | | |
| O | 8·0 | 3·78 | 5·34 | 4·70 | | | | |
| | 211·8 | 100·00 | 100·00 | 100·00 | | | | |

If the preceding formula be correct, the formation of the salt must be attended with evolution of oxygen and substitution of chlorine in its place.—Gerhardt, however, whose analytical results differ greatly from those of Raewsky, regards the salt as identical with the ammonio-bichloride of platinum (or bichlorhydrate of diplatinamine) discovered by Gros (O, p. 305). ¶

X. Fluoplatinate of Ammonium.—Dark brown, gummy, amorphous.—When treated with water, it is resolved into a soluble *acid* salt and an insoluble *basic* salt. Insoluble in alcohol. (Berzelius, *Lehrbuch.*)

Y. Ammonio-nitrate of Platinous Oxide.—*a. With 2 At. Ammonia.*—$2NH^3,PtO,NO^5$.—[Nitrate of Diplatosamine: $N^2H^5Pt,NHO^3$.]—*a. Yellow.*—When a solution of the chlorine-compound ($2NH^3,PtCl$) prepared by (1), is precipitated by nitrate of silver and the filtrate evaporated, neutral crystals are obtained. (Reiset.) The salt may be directly obtained by treating Reiset's chlorine-compound ($2NH^3,PtCl$) with nitric acid. In properties and composition, the crystals agree perfectly with the following salt β, but they are yellow. (Peyrone.)

β. *Colourless.*—Nitric acid added to the aqueous solution of the colourless chlorine-compound ($2NH^3,PtCl$) prepared by (2,) throws down

small needles; and when these are washed with alcohol, dissolved in boiling water, and the solution evaporated and cooled, the salt separates out in small, transparent, and colourless needles, which are soft to the touch and flexible. When heated, they deflagrate like gunpowder. Boiled with nitric acid and alcohol, they deposit a yellowish-white substance insoluble in water (containing 46·5 p. c. platinum and 2·9 hydrogen, and dissolving in nitric acid with formation of peculiar crystals), and give off a vapour which excites tears, acts strongly on the olfactory organ, and when condensed by cooling, forms with the solution of the undecomposed salt in nitric acid, a beautiful blue substance. (Peyrone.)

| | *Dried at* 100°. | | Peyrone. *α.* | *β.* |
|---|---|---|---|---|
| 3N | 42 | 21·54 | 21·68 | |
| 6H | 6 | 3·08 | 3·20 | 3·26 |
| Pt | 99 | 50·77 | 50·43 | 50·33 |
| 6O | 48 | 24·61 | | |
| $2NH^3,PtO,NO^5$ | 195 | 100·00 | | |

*b. With* 1 *At. Ammonia.*—$NH^3,PtO,NO^5$.—[Nitrate of Platosamine : $NH^2Pt,NHO^3$.]—Formed by boiling the iodine-compound ($NH^3,PtI$) with aqueous silver-nitrate, and evaporating the filtrate; the boiling must be continued for some time, inasmuch as the decomposition takes place but slowly. The salt crystallizes with difficulty, reddens litmus strongly, may be obtained in the anhydrous state, and is converted, by solution in ammonia, into the preceding salt *α*, *α*. (Reiset.)

Z. *Ammonio-nitrate of Platinic Oxide?*—Precipitated, according to Bergman, in the crystalline form, on mixing platinic nitrate with ammonia.

*a. With* 2 *At. Ammonia.*—The compounds: (*α.*) $2NH^3,PtO,NO^5 + Aq.$ = *Mononitrate of Diplatinamine*: $N^2H^4pt^2,NHO^3 + Aq.$,—and (*β.*) $2(2NH^3,PtO^2),3NO^5 + Aq.$ = *Sesquinitrate of Diplatinamine*: $2N^2H^4pt^2,3NHO^3 + Aq.$, have been obtained by Gerhardt (pp. 316, 317).

*b. With* 1 *At. Ammonia.*—(*α.*) $NH^3,PtO^2,NO^5 + 3Aq.$ = *Mononitrate of Platinamine* = $NHpt^2,NHO^3 + 2Aq.$; and (*β.*) $NH^3,PtO^2,2NO^5$ = *Binitrate of Platinamine* = $NH^2pt^2,2NHO^3$. (Gerhardt, p. 315.)

AA. Ammonio-nitrate of Oxychloride of Platinum.—Bichlorhydronitrate of Diplatinamine : $N^2H^4pt^2,NHO^3,ClH$.]—The green compound of Magnus ($NH^3,PtCl$) heated with nitric acid, first turns brown, and is afterwards converted into a mixture of platinum and a white crystalline powder, which is dissolved out by boiling water, and crystallizes on cooling. No other products are formed; only, after very long boiling, the nitric acid acquires a yellow colour, from the presence of platinum sal-ammoniac, which being much less soluble, may easily be separated from the white salt. (Gros.) The action probably takes place thus:

$$2(NH^3,PtCl) + HO + NO^5 = 2NH^3,PtClO,NO^5 + Pt + HCl.$$

Shining flattened prisms, colourless or pale yellow. The salt, when ignited with carbonate of soda, leaves a residue of platinum and chloride of sodium. With hydrate of lime, it gives off a small quantity of ammonia; with cold potash-ley, a larger quantity; and with boiling potash-ley, a very large quantity, being itself dissolved at the same time. If the boiling be continued till the evolution of ammonia ceases, a white powder separates, containing nitrogen, hydrogen, platinum, and oxygen, but no chlorine; this substance assumes a whitish-grey colour at 120°, detonates

at 250° with abundant formation of gas, and is soluble in sulphuric, nitric, and acetic acid, but not in water or ammonia. Alkaline carbonates form, with the aqueous solution of the nitrate, a white flocculent precipitate, which, after washing and drying, dissolves with effervescence in acids. Sulphuretted hydrogen passed through the aqueous solution, throws down, after some time, a small quantity of sulphur, coloured brownish-yellow from admixture of platinum; but the quantity of platinum thus precipitated does not exceed $\frac{1}{2}$ per cent. With nitrate of silver, the solution likewise exhibits a whitish turbidity after a while; on the application of heat, the precipitate increases, but its aspect is different from that of chloride of silver.

| | *Dried.* | | | Gros. |
|---|---|---|---|---|
| 3N | 42·0 | .... | 18·23 | |
| 6H | 6·0 | .... | 2·60 | ..... 2·77 |
| Pt | 99·0 | .... | 42·97 | ..... 42·35 |
| Cl | 35·4 | .... | 15·37 | ..... 15·49 |
| 6O | 48·0 | .... | 20·83 | |
| $2NH^3,PtClO,NO^5$ | 230·4 | .... | 100·00 | |

¶ According to Raewsky, the nitric acid salt W, discovered by Gros, is obtained only when the quantity of nitric acid used is reduced to the minimum, so that, in preparing this salt, it is best to add at first a quantity of nitric acid less than that required to complete the reaction, and afterwards supply the deficiency by small successive additions. When, on the contrary, the green salt of Magnus is treated with an excess of strong nitric acid, red fumes are evolved, and two nitrates are formed, containing respectively the bases $4NH^3,Pt^2ClO^5$ and $2NH^3,PtClO^2$; their formation is expressed by the following equation:

$$8(NH^3,PtCl)+24(NO^5,HO)=4NH^3,Pt^2ClO^5,2NO^5+2(2NH^3,PtClO^2,NO^5)+4(PtO^2,2NO^5)+19HO+5HCl+12NO^4.$$

BB. *Binitrate:*—$4NH^3,PtClO^5,2NO^5$.—This compound separates in the form of a white granular salt, which, after long boiling, and leaving the solution to cool a little, may be separated by decantation from the liquid, and then washed on a filter with a very small quantity of water. It is then dissolved in water nearly boiling, and the solution evaporated in vacuo over sulphuric acid. After four crystallizations, the salt is obtained in small, white, shining laminæ, or scales. After drying at 120°, it gives off water when heated, exploding slightly, yielding a sublimate of sal-ammoniac, and leaving metallic platinum. When boiled with potash, it turns yellow, and gives off ammonia. A small quantity of dilute sulphuric acid exerts no action upon it, but on the addition of copper turnings, red fumes are evolved. Nitrate of silver is not clouded by it.

| | *Dried at* 120°. | | | Raewsky. | | | |
|---|---|---|---|---|---|---|---|
| 6N | 84·0 | 18·69 | | 20·57 | 20·44 | 19·54 | 19·00 |
| 12H | 12·0 | 2·67 | | 2·72 | 2·76 | 2·73 | 2·73 |
| 2Pt | 198·0 | 44·07 | | 43·49 | 43·82 | 44·17 | 44·10 |
| Cl | 35·4 | 7·87 | | 7·65 | 7·68 | 8·00 | 8·00 |
| 15O | 120·0 | 26·70 | | 25·42 | 25·50 | 25·46 | 26·17 |
| $4NH^3,Pt^2ClO^5,2NO^5$ | 449·4 | 100·00 | | 99·85 | 100·20 | 99·90 | 100·00 |

[According to Gerhardt, this salt is a *Sesquichlorhydro-nitrate of Diplatinamine*: $N^2H^4pt^2,2NHO^3+N^2H^4pt^2,ClH$.]

CC. *Mononitrate.*—$2NH^3,PtClO^2,NO^5$.—The mother-liquid obtained in the preparation of the salt BB, contains a second platinum-salt, which

separates out when the liquid is decanted from the salt BB, and left to cool. The acid liquid again decanted from the new deposit, leaves, on evaporation and ignition, a very large quantity of platinum. Hence, to obtain the salt pure and crystallized, it is necessary to use a considerable quantity of platinum. When pure, it is perfectly white, and crystallizes in very small, shining needles. When heated, it decrepitates, gives off sal-ammoniac and water, and leaves platinum. Solution of potash colours it yellow, and, on boiling, dissolves it with evolution of ammonia. With sulphuric acid and copper, and with nitrate of silver, it behaves like BB.

| | *Crystallized.* | | | Raewsky. | |
|---|---|---|---|---|---|
| 3N | 42·0 | 17·61 | 17·90 | | |
| 6H | 6·0 | 2·52 | 2·43 | | 2·50 |
| Pt | 99·0 | 41·53 | 42·00 | | 42·20 |
| Cl | 35·4 | 14·85 | 14·58 | | 14·60 |
| 7O | 56·0 | 23·49 | 23·09 | | 22·80 |
| $2NH^3,PtClO^2,NO^5$ | 238·4 | 100·00 | 100·00 | | |

[According to Gerhardt: *Bichlorhydro-nitrate of Diplatinamine*: $N^2H^4pt^2,NHO^3,ClH$; identical with the salt AA, obtained by Gros.]

## Gerhardt's *Platinum-bases and General Theory of the Ammoniacal Compounds of Platinum.*

(*Comptes rendus des travaux en Chimie*, 1850, 273.)

The ammoniacal compounds of platinum are regarded by Gerhardt as containing certain bases or alkalis formed from ammonia by the substitution of one or two atoms of platinum for hydrogen, the platinum (like other metals, in the system of Laurent and Gerhardt) being moreover supposed to enter into its several compounds with two different atomic weights, viz. as *Platinosum* = Pt = 99, and as *Platinicum* = pt = 49·5; thus platinous oxide = PtO; platinic oxide = ptO.

According to this theory, Reiset's second base and its corresponding salts are supposed to contain an alkali, called *Platosamine* = $NH^2Pt$, in which 1 At. hydrogen is replaced by 1 At. platinosum; and Reiset's first base, with the corresponding salts, is supposed to contain another alkali, called *Diplatosamine* = $N^2H^5Pt$, formed by the union of 2 atoms of ammonia into one, and the substitution therein of 1Pt for 1H: thus:

Hydrochlorate of Platosamine = $NH^3,PtCl = NH^2Pt + HCl$.
Hydrochlorate of Diplatosamine = $2NH^3,PtCl = N^2H^5Pt + HCl$.

Similarly, by the substitution of 2pt for 2H in $NH^3$ and $N^2H^6$, two other bases are formed, viz. *Platinamine* = $NHpt^2$, and *Diplatinamine* = $N^2H^4pt^2$; thus:

Hydrochlorate of Platinamine = $NH^3,PtCl^2 = NHpt^2 + 2HCl$.
Hydrochlorate of Diplatinamine = $2NH^3,PtCl^2 = N^2H^4pt^2 + 2HCl$.

Platinamine and several of its salts have been prepared and investigated by Gerhardt, and will be described immediately. Bi-hydrochlorate of diplatinamine is the salt O, prepared by Gros (p. 305). The other salts obtained by Gros (*e.g.* T, V, and AA, pp. 309, 311), and hitherto supposed to contain a chloriferous base, PtClO, are regarded by Gerhardt as double salts containing hydrochloric acid together with another acid. Raewsky's salts (pp. 309, 312) are double salts of a similar character, but having their acids in different proportions.

A. Platinamine.—$NHpt^2$.—This compound is obtained in the form of shining, hydrated crystals, on treating a boiling solution of the nitrate with excess of ammonia. The crystals, which adhere strongly to the sides of the vessel, are separated from the liquid by decantation, and then boiled with water, which causes them to separate and collect at the bottom of the vessel in the form of a heavy crystalline powder, having a yellow colour and strong lustre. The ammoniacal mother-liquor yields a fresh crop of crystals on evaporation. The crystals, when examined by the microscope, present the form of small, very short rhomboidal prisms, often having their edges and angles modified. They suffer no loss of weight at 130°.

| | *Dried at* 130°. | | Gerhardt. |
|---|---|---|---|
| Pt | 99 | 66·00 | 65·66 |
| 5H | 5 | 3·33 | 3·36 |
| N | 14 | 9·33 | 9·70 |
| 2O | 32 | 21·34 | 21·28 |
| $NHpt^2 + 2Aq.$ | 150 | 100·00 | 100·00 |

The atomic weights used in the calculation of the preceding formula, and also in those of the following compounds, are: H = 1, N = 14, Cl = 35·5, Pt = 99, pt = 49·5, O = 16, S = 32. The same analysis calculated according to the atomic weights used in this work, leads to the formula $NH^3,PtO^2 + 2Aq$.

Platinamine decrepitates when heated in a closed tube, giving off water and ammonia, and leaving a residue of platinum. It dissolves readily in hot dilute acids, even in acetic acid. Boiling potash neither dissolves it nor separates ammonia from it. Platinamine combines with a great number of acids, forming crystallizable salts, some of which are neutral and others acid.

B. Sulphate of Platinamine.—$NHpt^2,SO^4H^2$.—Platinamine dissolves readily in dilute sulphuric acid; and when the solution is concentrated, crystalline pellicles of the sulphate separate on the surface. On evaporating to dryness, washing the residue with alcohol, and then drying it, the salt is obtained in the form of a yellow powder, having an acid taste, and dissolving with tolerable facility in warm water. The analyses of this salt dried at 120°, give 46·00 per cent. of platinum; the above formula requires 46·69. According to the atomic weights usually adopted, the formula of the salt is $NH^3,PtO^2,2SO^3$.

C. Bi-hydrochlorate of Platinamine.—$NHpt^2,2HCl$.—Obtained by the action of chlorine on hydrochlorate of platosamine, $NH^2Pt,HCl$ (the chlorine-compound of Reiset's second series, N, *b*, *a*, page 302). When this latter salt is suspended in water through which chlorine gas is passed, it is converted into a heavy, lemon-yellow powder, consisting of octohedral crystals, apparently with square or rectangular bases; they are insoluble in cold water, and very slightly soluble in boiling water or in water acidulated with hydrochloric acid.

| | *Crystallized.* | | Gerhardt. | |
|---|---|---|---|---|
| Pt | 99 | 52·94 | 52·67 | 52·88 |
| 3H | 3 | 1·60 | 1·77 | |
| 2Cl | 71 | 37·97 | 38·09 | |
| N | 14 | 7·49 | 7·43 | |
| $NHpt^2,2HCl$ | 187 | 100·00 | 99·96 | |

[This compound may also be regarded as an *ammonio-bichloride of platinum*, $NH^3,PtCl^2$; in fact, it bears the same relation to the compound O, p. 305, as N, *b* bears to N, *a*.]

Bi-hydrochlorate of platinamine is converted, by boiling with ammonia and subsequent evaporation, into bi-hydrochlorate of diplatinamine (the chlorine-compound of Gros' series, O, p. 305):

$$NHpt^2,2HCl + NH^3 = N^2H^4pt^2,2HCl.$$

It is not affected by strong sulphuric or nitric acid, even at a boiling heat; neither does a solution of bichloride of platinum exert any action upon it. When boiled with caustic potash, it does not give off ammonia, but dissolves, and forms a golden-yellow liquid, from which acids throw down a yellowish precipitate insoluble in acetic acid, and possessing properties different from those of platinamine.

D. Nitrate of Platinamine.—*a. Neutral.*—$NHpt^2,NHO^3 + 2Aq.$—Obtained by boiling the bi-hydrochlorate diffused through a large quantity of water with nitrate of silver, as long as chloride of silver continues to form. If the liquid be then filtered boiling hot, the nitrate separates on cooling in the form of a yellowish crystallo-granular powder, which, when examined by the microscope, appears to consist of rhombic or hexagonal tables. The yellowish solution reddens litmus, gives with potash or ammonia a precipitate of platinamine; with carbonate of soda, a yellowish white crystalline precipitate; and with phosphate of soda, a white flocculent precipitate, soluble in excess of the precipitant. Hydrochloric acid added to the solution of this salt, forms no precipitate in the cold, but, on the application of a gentle heat, throws down a precipitate of bi-hydrochlorate of platinamine.

| | *Dried at* 120°. | | | Gerhardt. | |
|---|---|---|---|---|---|
| Pt | 99 | 46·47 | 46·33 | 46·27 | |
| $H^6$ | 6 | 2·81 | 2·84 | 3·03 | |
| $N^2$ | 28 | 13·14 | 13·00 | | |
| $O^5$ | 80 | 37·58 | 37·83 | | |
| $NHpt^2,NHO^3 + 2Aq.$ | 213 | 100·00 | 99·84 | | |

[This salt may also be regarded as an ammonio-nitrate of platinic oxide; $NH^3,PtO^2,NO^5 + 3Aq.$, *vid.* p. 311.]

*b. Binitrate.*—$NHpt^2,2NHO^3$.—Obtained by mixing the solution of the preceding salt with excess of nitric acid, and evaporating. It forms a crystalline mass, which, after drying, presents the appearance of a yellowish powder.

| | | | Gerhardt. | |
|---|---|---|---|---|
| Pt | 99 | 41·25 | 41·17 | 41·25 |
| $H^3$ | 3 | 1·25 | 1·40 | |
| $N^3$ | 42 | 17·50 | 17·42 | |
| $O^6$ | 96 | 40·00 | 39·85 | |
| $NHpt^2,2NHO^3$ | 240 | 100·00 | 99·84 | |

[May also be regarded as $NH^3,PtO^2,2NO^5$].

E. Diplatinamine.—$N^2H^4pt^2$.—Not yet obtained in the separate state. It contains the elements of platinamine and ammonia, so that its salts might be regarded as double salts of those two bases. This mode of viewing them is supported by the circumstance that a great number of these salts are acid salts and contain two acids; so that if we suppose them also to contain two bases, their constitution will be that of neutral salts. Such a theory, however, would destroy all analogy between the ammoniacal compounds of the protochloride and bichloride of platinum, inasmuch as there would then be only one base corresponding to the bichloride.

Diplatinamine forms three kinds of salts, viz. mono-acid, sesqui-acid, and bi-acid salts, and exhibits a peculiar tendency to form double salts containing two acids. To the latter class, belong the salts discovered by Gros, and also those more recently discovered by Raewsky. The general formula of Gros' salts is that of bi-hydrochlorate of diplatinamine, in which half the hydrochloric acid is replaced by another acid, AcH, containing the same quantity of basic hydrogen:

$$\left.\begin{matrix}AcH\\ClH\end{matrix}\right\}N^2H^4pt^2.$$

This formula may also be doubled and thus written:

$$\left.\begin{matrix}2AcH,\ N^2H^4pt^2\\ 2ClH,\ N^2H^4pt^2\end{matrix}\right\}$$

In Raewsky's salts, Gerhardt finds, from his own analyses, the same elements, *minus* 1 eq. of hydrochloric acid; so that their general formula is

$$\left.\begin{matrix}2AcH,\ N^2H^4pt^2\\ ClH,\ N^2H^4pt^2\end{matrix}\right\}$$

Which may also be written:

$$\left.\begin{matrix}AcH\\ \frac{1}{2}ClH\end{matrix}\right\}N^2H^4pt^2.$$

According to this view, in short, *the salts discovered by Raewsky are sesqui-acid salts of diplatinamine, and those discovered by Gros are bi-acid salts of the same base.*

F. Hydrochlorate of Diplatinamine.—*a. Mono-acid.*—$N^2H^4pt^2$, HCl?—Chloroplatinate of ammonium digested in strong caustic ammonia dissolves, and forms a nearly colourless solution, from which alcohol throws down white flakes, which dry up to a pale yellow, resinous mass easily soluble in water. Its analysis leads to the formula $PtClN^2H^5$ (Laurent and Gerhardt, *Compt. rend. trav. Chim.* 1849, 113), which agrees numerically with that of a mono-hydrochlorate of diplatinamine. The addition of hydrochloric acid, however, does not convert it into the bi-hydrochlorate of that base; and altogether its reactions are such as to leave its rational constitution a matter of uncertainty.

*b. Bi-acid.*—$N^2H^4pt^2$,2HCl.—This salt is identical with the ammonio-bichloride of platinum $2NH^3,PtCl^2$, obtained by Gros (O, *p.* 305); also with the salt to which Raewsky assigns the formula, $Pt^2N^4H^{12}Cl^2O^2,Cl^2$ (*p.* 310); according to Gerhardt, this latter formula is based upon an incorrect analysis.

G. Nitrate of Diplatinamine. — *a. Mononitrate.* — $N^2H^4pt^2$, $NHO^3$ + Aq.—Formed by boiling the solid sesquinitrate (*b*) with ammonia, which dissolves it, and, on cooling, deposits the mononitrate in the form of a white amorphous powder, insoluble in cold water, but dissolving with tolerable facility in hot water.

| | *Dried at* 130°. | | Gerhardt. |
|---|---|---|---|
| Pt | 99 | 46·69 | 46·63 |
| 7H | 7 | 3·30 | 3·32 |
| 3N | 42 | 19·81 | 20·24 |
| 4O | 64 | 30·20 | 30·11 |
| $N^2H^4pt^2,NHO^3$ + Aq. | 212 | 100·00 | 100·00 |

[May also be regarded as an ammonio-nitrate of platinic oxide = $2NH^3,PtO^2,NO^5$ + Aq.]

This salt explodes violently and with ignition when heated in a tube. When moistened in the dry state with sulphuric acid, it assumes a blue

colour, and emits red vapours. A tolerably concentrated solution forms, with oxalate of ammonia, a heavy, white, crystalline precipitate, composed of small prisms; with phosphate of soda, a white flocculent precipitate, soluble in excess of the phosphate; with sulphate of soda, no precipitate; with carbonate of soda, a white crystalline precipitate, having but little density; with sal-ammoniac, no precipitate; with hydrochloric acid, nothing at ordinary temperatures; but if the liquid be boiled and left to cool, a light crystalline white precipitate is formed, consisting of octohedrons of the bi-hydrochlorate.

*b. Sesquinitrate.*—$2N^2H^4pt^2,3NHO^3 + Aq.$—Obtained by the action of hot concentrated nitric acid on nitrate of diplatosamine (Y, *p.* 310). The crystals of the latter salt, when thus treated, are converted into a blue powder, which however loses its colour after continued boiling. On decanting the nitric acid, dissolving the powder in boiling water, and leaving the liquid to cool, the sesquinitrate separates in the form of a white crystalline powder, which, when examined by the microscope, appears to be composed of hexagonal tables and very oblique prisms with hexagonal bases.

| | | | | | Gerhardt. |
|---|---|---|---|---|---|
| 2Pt | 198 | .... | 42·21 | .... | 42·00 |
| 13H | 13 | .... | 2·77 | .... | 2·88 |
| 7N | 98 | .... | 20·90 | .... | 21·18 |
| 10 O | 160 | .... | 34·12 | .... | 33·94 |
| $2N^2H^4pt^2,3NHO^3 + Aq.$ | 469 | .... | 100·00 | .... | 100·00 |

[May also be regarded as *ammonio-sesquinitrate of platinic oxide* = $4NH^3,2PtO^2,3NO^5 + Aq.$

Sesquinitrate of diplatinamine is slightly soluble in cold water; boiling water dissolves it more freely, but the greater part separates again in the crystalline state on cooling. It is less soluble in nitric acid than in water. When heated in a closed tube, it explodes suddenly like an azotized organic body.

A saturated aqueous solution of this salt gives no precipitate with potash or ammonia, either in the cold or when heated; with carbonate of soda, a white crystalline precipitate; with carbonate of ammonia, after a few seconds, flakes and crystalline pellicles form on the surface of the liquid, presenting under the microscope the appearance of interlacing needles; with oxalate of ammonia, an abundant white, flocculent precipitate; with sulphate or phosphate of soda, no precipitate; with hydrochloric acid, after a few moments, a heavy, white, crystalline precipitate, which becomes more abundant on boiling, and when examined by the microscope, presents the appearance of small prisms; no precipitate with sal-ammoniac or sulphuric acid; with nitric acid, after a few seconds, a white crystalline precipitate.

H. Sesquichlorhydro-carbonate of Diplatinamine.—*Raewsky's Carbonate* (p. 309). — Gerhardt assigns to this salt, the formula: $N^2H^4pt^2,CO^3H^2 + N^2H^4pt^2,ClH + Aq.$

| | | | | | Raewsky. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2Pt | 198·0 | .... | 53·3 | .... | 49·00 | .... | 49·70 | .... | 49·75 |
| 13H | 13·0 | .... | 3·4 | .... | 2·97 | .... | 3·00 | .... | 3·00 |
| Cl | 35·5 | .... | 9·3 | .... | 9·00 | .... | 9·00 | | |
| 4N | 56·0 | .... | 14·7 | .... | 14·70 | | | | |
| C | 12·0 | .... | 3·1 | .... | 2·98 | .... | 3·00 | .... | 3·00 |
| 4O | 64·0 | .... | 16·2 | .... | 21·35 | | | | |
| | 378·5 | .... | 100·0 | .... | 100·00 | | | | |

The quantities of platinum determined by Raewsky's analyses are too low for the above formula; but Gerhardt is of opinion that the platinum-determinations made by Raewsky, not only in this but in all the other salts which he analyzed, are too low, the error arising from the mode of analysis employed, which was to calcine the salt with carbonate of soda and then separate the platinum by filtration. This method, according to Gerhardt, always involves a loss of platinum; whereas if the salt be calcined with merely the addition of a few drops of strong sulphuric acid, the calcination may be effected without the slightest projection, and a very exact result obtained. — Raewsky's platinum-determinations are too small even for his own formula— $4NH^3,Pt^2ClO^5,2CO^2$—which requires 51·2 per cent. of platinum.

I. Sesquichlorhydro-phosphate of Diplatinamine. — *Raewsky's Phosphate* (p. 309).—Gerhardt's formula for this salt is: $N^2H^4pt^2,PO^4H^3 + N^2H^4pt^2,ClH$.

| | | | | Raewsky. | | |
|---|---|---|---|---|---|---|
| 2Pt | 198·0 | 49·9 | | 47·20 | 47·10 | 46·9 |
| 12H | 12·0 | 3·0 | | 2·70 | 2·78 | 2·8 |
| Cl | 35·5 | 8·9 | | 7·84 | 7·96 | 8·0 |
| 4N | 56·0 | 14·1 | | 13·40 | 13·43 | |
| P | 32·0 | 8·0 | | 7·38 | 7·46 | |
| 4O | 64·0 | 16·1 | | 21·48 | 20·27 | |
| | 397·5 | 100·0 | | 100·00 | 100·00 | |

Raewsky's formula, $4NH^3,Pt^2ClO^5,PO^5,HO$, requires 46·80 p.c. platinum, 3 hydrogen, 8·4 chlorine, 13·28 nitrogen, and 7·58 phosphorus.

K. Bichlorhydro-sulphate of Diplatinamine. — *Gros' Sulphate* (V, pp. 309, 310).—To this salt Gerhardt assigns the formula: $N^2H^4pt^2,SO^4H^2 + N^2H^4pt^2,2ClH$.

Gerhardt has likewise obtained this compound by dissolving the bi-hydrochlorate of diplatinamine in strong sulphuric acid, and heating to volatilize part of the acid. A large quantity of hydrochloric acid was disengaged; and, on cooling, a crystalline mass was obtained, which, by solution in boiling water and cooling, was converted into a crystalline powder composed of very short prisms. This salt yielded 45·21 per cent. of platinum, which agrees very nearly with that in the salt prepared by Gros (*p.* 309).

L. Chlorhydro-nitrate of Diplatinamine. — *a. Sesqui-acid.* — When bi-hydrochlorate of diplatinamine is boiled for a few minutes with solution of nitrate of silver, and the liquid filtered at a boiling heat, the filtrate, on cooling, deposits a yellowish crystalline mass, which may be purified by recrystallization from hot water; it then forms small, hard, shining, rhombic tables. If too small a quantity of nitrate of silver be used in the preparation, the product consists wholly of the bi-acid salt *b*.

| | *Dried at* 120°. | | Gerhardt. | |
|---|---|---|---|---|
| 2Pt | 198·0 | 44·75 | 44·67 | 44·67 |
| 13H | 13·0 | 2·93 | 2·94 | |
| Cl | 35·5 | 8·02 | 8·24 | 8·00 |
| 6N | 84·0 | 18·98 | 18·92 | |
| 7O | 112·0 | 25·32 | 25·23 | |
| $2NHO^3,N^2H^4pt^2$ / $ClH,N^2H^4pt^2$ + Aq. | 442·5 | 100·00 | 100·00 | |

This salt is identical with one of the nitrates obtained by Raewsky (BB, *p.* 312), to which that chemist assigns the formula $4NH^3,Pt^2ClO^5,2NO^5$. By reference to the analyses given on page 312, it will be seen that

Raewsky's numbers approach very nearly to those of Gerhardt, excepting in the platinum, in which, for the reason already stated (p. 318), Raewsky's determinations are too low. Moreover, Gerhardt analyzed a specimen of the salt prepared by Raewsky himself, and found it to contain 44·67 per cent. of platinum and 2·96 of hydrogen, the same as in the analysis above given.

A solution of sesquichlorhydro-nitrate of diplatinamine yields, with oxalate of ammonia, a white crystalline precipitate of the bichlorhydrate, which assumes a very light yellow colour when dry; with carbonate of soda it forms a white curdy precipitate. With phosphate of soda, no immediate precipitate is formed; but on agitation with a glass rod, white crystalline flakes are produced; and on rubbing the sides of the tube with the rod, striæ appear, as with the ammonio-magnesian phosphate. A solution of the salt gives no precipitate with sulphate of soda; but if the mixture be left to stand for 24 hours, a few crystalline flakes appear.

*b. Bi-acid.*—$N^2H^4pt^2,NHO^3,ClH$.—This salt is identical with the nitrate, $NH^3,PtClO,NO^5$, obtained by Gros (AA, p. 311). Raewsky's nitrate of the mother-liquid (CC, p. 312), to which he assigns the formula $2NH^3,PtClO^2,NO^5$, is likewise the same salt, as may be seen by comparing the analysis given on page 313 with that of Gros' salt AA.

M. Bichlorhydro-chloroplatinate of Diplatinamine. — The green salt of Magnus is regarded by Gerhardt as chloroplatinate* of diplatosamine, $N^2H^5Pt,PtHCl^3$; and the yellow compound isomeric with it (the chlorine-compound of Reiset's second series), as hydrochlorate of platosamine, $NH^2Pt,HCl$. As the latter, under the influence of chlorine, forms a salt of platinamine, so likewise the former, when similarly treated, yields a salt of diplatinamine, the chloroplatinous acid being at the same time converted into chloroplatinic acid. By passing chlorine gas through water in which the green compound is suspended, the latter is converted into a red, shining, crystalline powder, which is the chloroplatinate of diplatosamine, $N^2H^5Pt,PtHCl^3$, previously obtained by Reiset. The liquid acquires a red colour, and, if the stream of chlorine be continued, the red compound first produced is partly dissolved, and partly converted into a yellowish white crystalline precipitate. If the action of the chlorine be discontinued as soon as the red body has entirely disappeared, the liquid then evaporated, and alcohol added, the bichlorhydro-chloroplatinate of diplatinamine separates out in the form of shining yellow needles or prisms. It dissolves readily in hot water.

| | *Dried at* 120°. | | Gerhardt. |
|---|---|---|---|
| 2Pt | 198 | 51·69 | 51·50 |
| 7H | 7 | 1·82 | 1·96 |
| 4Cl | 142 | 37·07 | 37·23 |
| 2N | 28 | 7·31 | 7·60 |
| ½O | 8 | 2·11 | 1·71 |
| $\left.\begin{matrix}PtCl^3H\\ClH\end{matrix}\right\}N^2H^4pt^2+\frac{1}{2}Aq.$ | 383 | 100·00 | 100·00 |

If the action of the chlorine be too long continued, the salt just described is attacked in its turn, and hydrochloric acid is produced, which then gives rise to the formation of a certain quantity of bi-hydrochlorate of diplatinamine and bichloride of platinum. ¶

* In Gerhardt's nomenclature, *chloroplatinous acid* is the compound of platinous chloride with hydrochloric acid; *chloroplatinic acid*, the compound of platinic chloride with hydrochloric acid.

## Platinum and Potassium.

A. Alloy of Platinum and Potassium.—The two metals unite very readily, exhibiting incandescence, and forming a shining brittle mass. This substance, when heated in the air, burns, and leaves a yellow powder, which gives off oxygen when heated. The yellow substance is likewise decomposed by water.

B. Platinite of Potash.—1. Hydrate of potash fused with platinum in a close vessel yields platinite of potash, which forms a blackish green solution in water. (Berzelius.)—2. When protochloride of platinum is decomposed by aqueous potash, part of the resulting protoxide dissolves in the potash, forming a black solution, which appears dark green when diluted. (Berzelius.)

C. Platinate of Potash.—1. The yellow powder formed by the combustion of the alloy of platinum and potassium, reddens turmeric paper, even after washing for any length of time; it appears, indeed, to be a compound of platinic oxide with potash. (H. Davy.)

2. When platinum is heated with nitre, there are formed: (*a*), a brown compound of platinic oxide with a small quantity of potash, insoluble in water; (*b*), a compound which dissolves in water and forms a yellowish brown solution; acids added to this solution precipitate the platinic oxide in combination with small quantities of potash and acid. (Tennant, *Scher. J.* 1, 308.)

When platinum is fused with hydrate of potash and nitre, and the product washed with water, there remains a partly purple, partly yellowish oxide, which dissolves with difficulty in hydrochloric acid, leaving a residue of platinum. Chloroplatinate of potassium boiled down with a large quantity of strong potash, forms a yellow liquid, which dries up to a scarlet-coloured mass. When this mass is heated not quite to redness, and the chloride of potassium and excess of potash dissolved out, there remains a rusty-coloured compound of platinic oxide and potash, which runs through the filter like a yellow milk, unless some salt be added to the wash-water. It contains 7 per cent. of potash. It does not dissolve in hot oil of vitriol or nitric acid, even after several hours' digestion; the acids, however, dissolve out the potash. It likewise gives up its potash to cold hydrochloric acid. In tolerably strong hydrochloric acid it dissolves gradually, forming a solution of chloroplatinate of potassium and free bichloride of platinum. At an incipient red heat, the platinic oxide gives up half its oxygen, so that a dark-coloured platinite of potash is left behind. Platinate of potash detonates violently with combustible matters. When the above-mentioned scarlet mass is heated till it is brought into a state of red-hot fusion, it no longer appears red on cooling, but of a dingy yellow colour, inclining to greenish-brown, and after washing with water leaves a darker greenish-yellow compound of 1 At. potash with 5 At. platinum, and such a quantity of oxygen, that 1 At. platinum is combined with more than $1\frac{1}{2}$ At., but not quite 2 At. oxygen; at a red heat, it gives off water and oxygen, and leaves platinite of potash. The reddish yellow solution of the unignited compound in warm hydrochloric acid, when mixed with a larger quantity of chloride of potassium, yields, not only chloroplatinate of potassium, but ultimately also, crystals of chloroplatinite of potassium. (Berzelius, *Jahresber*, 9, 110.)

D. Sulphide of Platinum and Potassium.—When bisulphide of potassium is fused in a platinum crucible, a compound of protosulphide of potassium with sulphide of platinum is formed. This compound is green, and when dissolved in water, leaves a red-brown residue of sulphide of platinum. (Berzelius, *Schw.* 34, 22.)

*Aqueous.*—Sulphide of platinum precipitated by sulphuretted hydrogen, dissolves easily in hydrosulphate of potash. (Berzelius.)

¶ E. Sulphite of Platinous Oxide and Potash.—$3(KO,SO^2) + PtO,2SO^2 + 2\frac{1}{2}HO$. — Chloroplatinate of potassium heated with a solution of sulphite of potash, forms a solution which becomes colourless after a while, and, on evaporation, deposits the double salt in the form of a white precipitate. Hydrochloric acid reconverts it into chloroplatinate of potassium, with evolution of sulphurous acid.

| | | | | | Claus. |
|---|---|---|---|---|---|
| $3KO$ | 141·6 | .... | 34·66 | .... | 34·50 |
| $5SO^2$ | 160·0 | .... | 39·16 | .... | 39·77 |
| Pt | 99·0 | .... | 24·22 | .... | 24·25 |
| O | 8·0 | .... | 1·96 | .... | 1·48 |
| $3(KO,SO^2) + PtO,2SO^2$ | 408·6 | .... | 100·00 | .... | 100·00 |

(Claus, *Ann. Pharm.* 63, 359.) ¶

F. Sulphate of Platinous Oxide and Potash?—When a mixture of sulphate of potash and platinous sulphate prepared by method (2) (p. 289) is evaporated, the liquid becomes decolorized, and a dark bottle-green precipitate is produced, which appears black and shining when washed and dried, and at a red heat, gives off sulphurous and sulphuric acid, leaving a residue of platinum mixed with sulphate of potash. (Vauquelin.)

G. Sulphate of Platinic Oxide and Potash. — *Basic.* — When platinic sulphate is mixed with potash till the acid reaction is destroyed, and the liquid boiled for a few minutes, it becomes colourless, and deposits this double salt, which is black-brown, strongly lustrous, tasteless, and permanent in the air. It contains 78·32 platinic oxide, 10·84 sulphate of potash, and 10·84 water. At a red heat, it gives off oxygen gas, and is reduced to a mixture of platinum and sulphate of potash. Dissolves readily in boiling hydrochloric acid; is slightly decomposed by aqua-regia; not attacked by boiling nitric, sulphuric, phosphoric, or acetic acid, or by ammonia. (E. Davy.)

H. Iodoplatinate of Potassium.—A solution of biniodide of platinum in aqueous iodide of potassium is left to crystallize, and the crystals freed from adhering iodide of potassium by digestion in alcohol of 36°. (Lassaigne, *J. Chim. méd.* 8, 715.)—2. Aqueous bichloride of platinum is evaporated nearly to dryness with a slight excess of iodide of potassium, and the residue washed with alcohol as long as it colours the liquid. (Mather, *Sill. Am. J.* 27, 257.)

Black, rectangular tables, with four-sided pyramids attached; permanent in the air. (Lassaigne.) Black grains. (Mather.) Gives off part of its iodine when heated above 100°. (Lassaigne.) At a red heat, it leaves 50·89 per cent. of platinum and iodide of potassium. (Mather.) Not decomposed by oil of vitriol. (Lassaigne.) Dissolves very easily in water, forming a solution of a fine wine-red colour. A very dilute

solution soon turns brown, especially when exposed to light, and deposits steel-grey biniodide of platinum on the sides of the vessels. (Lassaigne.) This compound is precipitated after a few minutes in the form of a black powder, while the liquid becomes decolorized. (Mather.) Insoluble, or but very slightly soluble, in absolute alcohol. (Lassaigne.)

| | | | Lassaigne. | Mather. | Kane.* |
|---|---|---|---|---|---|
| KI | 165·2 | 32·00 | 31·99 | 50·89 | 38·75 |
| Pt | 99·0 | 19·18 | 68·01 | | 23·75 |
| 2I | 252·0 | 48·82 | | 49·11 | 37·50 |
| KI,PtI² | 516·2 | 100·00 | 100·00 | 100·00 | 100·00 |

* The salt examined by Kane (*Phil. Mag. J.* 2, 198) was obtained in the form of a black powder by agitating an excess of pulverized iodide of potassium with a concentrated solution of bichloride of platinum and a small quantity of ether, and collecting the precipitate on a filter. It dissolved easily in water, forming a wine-red liquid which was not decomposed by evaporation; it was also soluble in potash-ley and in alcohol, but not in ether. Kane supposes that it contains a sesqui-iodide of platinum.

I. Bromoplatinate of Potassium.—Formed by adding aqueous bromide of potassium to aqueous bi-bromide of platinum. If the solutions are somewhat concentrated, the compound is precipitated in the form of a granular cochineal-coloured powder; but from a more dilute solution, it separates, on evaporation by heat, in very beautiful red crystals, and on spontaneous evaporation, in regular octohedrons and cubo-octohedrons. The salt decrepitates when heated, acquiring at the same time a darker colour, and is decomposed, with evolution of bromine vapour. It is sparingly soluble in water; insoluble in alcohol. (Bonsdorff, *Pogg.* 19, 344; 33, 61.)

| | *Crystallized.* | | Bonsdorff. |
|---|---|---|---|
| KBr | 117·6 | 31·50 | 31·03 |
| Pt | 99·0 | 26·51 | 26·06 |
| 2Br | 156·8 | 41·99 | |
| KBr,PtBr² | 373·4 | 100·00 | |

K. Chloroplatinite of Potassium.—A solution of the brown protochloride of platinum in hydrochloric acid, mixed with chloride of potassium, yields red, anhydrous prisms, which dissolve easily in water, forming a reddish yellow solution, but are insoluble in alcohol, and are therefore precipitated by alcohol from the aqueous solution, in soft, rose-coloured crystalline fibres. (Magnus, *Pogg.* 14, 241.)

| | *Crystallized.* | | Magnus. |
|---|---|---|---|
| KCl | 74·6 | 35·69 | 35·79 |
| Pt | 99·0 | 47·37 | 46·74 |
| Cl | 35·4 | 16·94 | 17·47 |
| KCl,PtCl | 209·0 | 100·00 | 100·00 |

Sulphite of potash added to a cold aqueous solution of bichloride of platinum forms a yellow precipitate of chloroplatinate of potassium; but on the application of heat, the precipitate dissolves, and the decolorized liquid, when evaporated and cooled, deposits white crystalline grains, sparingly soluble in cold water; more readily in hot water. (Berthier, *N. Ann. Chim. Phys.* 7, 82.)

L. Chloroplatinate of Potassium.—Precipitated in the form of a lemon-yellow, crystalline powder, on mixing an aqueous solution of bichloride of platinum with potash or a potash-salt; crystallizes from its

aqueous solution in orange-coloured octohedrons. When very strongly heated, it is reduced to a mixture of platinum and chloride of potassium, giving off nothing but a little decrepitation-water, and the chlorine which was combined with the platinum. (Berzelius.) When the salt is heated to a temperature somewhat below its melting point, it is but partially decomposed, and the separated platinum remains, after washing with water, in the form of a black powder. If, on the contrary, it be fused for an hour, the whole of the platinum, probably from welding together of the powder, is converted into shining laminæ, which, as the chloride of potassium volatilizes, unite into a network; but even after long fusion, part of the chloroplatinate of potassium remains undecomposed, and dissolves in hot water together with the chloride of potassium. (Jacquelain, *Ann. Chim. Phys.* 74, 213; also *J. pr. Chem.* 22, 22.) When the salt is heated in a current of hydrogen gas, complete decomposition ensues. (Berzelius.) On heating this salt with hydrate of potash and a small quantity of water, a clear liquid is formed, which at an incipient red heat is decomposed, with separation of platinic oxide. The salt dissolves sparingly, and with a pale yellow colour, in water and in aqueous acids, somewhat more freely when heated, and still more abundantly in aqueous potash. From a hot saturated solution in caustic potash, it does not separate on cooling, except on the addition of hydrochloric acid. (H. Rose.) It dissolves very easily in a moderately warm solution of aqueous hyposulphite of soda mixed with a little free soda; if the hyposulphite of soda is in excess, and hydrochloric acid is added to it, the platinum is completely precipitated on the application of heat. (Himly, *Ann. Pharm.* 43, 152.)

| | | | | Berzelius. | | Warzer. |
|---|---|---|---|---|---|---|
| KCl | 74·6 | 30·52 | | 30·58 | | 29·6 |
| Pt | 99·0 | 40·51 | | 40·43 | | |
| 2Cl | 70·8 | 28·97 | | 28·99 | | |
| $KCl,PtCl^2$ | 244·4 | 100·00 | | 100·00 | | |

M. Fluoplatinate of Potassium.—Formed by precipitating hydrofluate of potash with less than the equivalent quantity of bichloride of platinum, decanting the liquid from the chloroplatinate of potassium, and evaporating. A dark brown deliquescent salt then separates, which is insoluble in alcohol. (Berzelius, *Pogg.* 1, 36.)

N. Nitrate of Platinic Oxide and Potash.—*Basic.*—Potash added to a solution of platinic nitrate, throws down the first half of the oxide as a pure hydrate, and the remainder in the form of a lighter brown, basic double salt. (Berzelius.)

## Platinum and Sodium.

A. Alloy of Platinum and Sodium.—Behaves like the alloy of platinum and potassium. (H. Davy.)

B. Platinite of Soda.—When protochloride of platinum is decomposed by excess of soda, part of the protoxide dissolves in the soda. From the colourless solution, nitric acid throws down a white, very bulky protoxide, which turns bluish grey when exposed to sunshine, and deep black when heated—is decomposed by heat, yielding 15 per cent. of oxygen

gas—and before drying, is soluble without colour in excess of nitric acid. (Vauquelin.)

C. Platinate of Soda.—From a clear aqueous mixture of bichloride of platinum and carbonate of soda, exposed to sunshine, or heated to 100°, platinate of soda is deposited in a few days, in the form of a reddish yellow, partly pulverulent, partly crystalline precipitate. (W. Döbereiner, *Pogg.* 28, 180.) If the solutions of the two salts are used in as concentrated a state as possible, the mixture boiled down to dryness, and the residue washed with water, a denser precipitate is obtained, having more of an ochre-yellow colour. (Fr. Weiss & Fr. Döbereiner, *Ann. Pharm.* 14, 21.)

| | | | | Weiss & Döbereiner. |
|---|---|---|---|---|
| $NaO$ | 31·2 | 7·25 | | 7·44 |
| $3PtO^2$ | 345·0 | 80·20 | | 79·99 |
| $6HO$ | 54·0 | 12·55 | | 12·50 |
| $NaO,3PtO^2+6Aq.$ | 430·2 | 100·00 | | 99·93 |

At a red heat, it first gives off water, afterwards oxygen gas, and leaves a black residue, from which the soda may be dissolved out by water. The residual black powder appears to be a mixture of platinum and platinic oxide; at all events, hydrochloric acid dissolves out platinic oxide from it. Formic acid, with the aid of heat, converts platinate of soda into platinum-black, causing at the same time a brisk evolution of carbonic acid and formation of formiate of soda (p. 278). Heated aqueous oxalic acid dissolves platinate of soda, with evolution of carbonic acid, forming a dark liquid, which, on cooling, first becomes green and then dark blue, and deposits copper-coloured needles of platinous oxalate. Acetic acid withdraws all the soda from platinate of soda, together with a small quantity of platinic oxide, and leaves pure, ochre-yellow hydrate of platinic oxide. Dilute nitric acid dissolves it easily and completely, forming a deep yellow liquid, which forms, with nitrate of silver, a yellow precipitate, soluble in nitric acid. (W. Döbereiner.) Dilute oxygen-acids extract the soda without dissolving the platinic oxide; from the denser ochre-yellow compound, strong nitric acid dissolves out nothing but soda. (Fr. Weiss & Fr. Döbereiner.)

D. Borax forms, with the platinous oxide prepared by E. Davy (p. 282), a black glass, which afterwards becomes coloured from reduction of platinum.

E. Sulphoplatinate of Sodium.—1. When chloroplatinate of ammonium is fused with an equal weight of sulphur and ignited carbonate of soda, a mass is obtained, which dissolves in water, forming a very deep red solution, while part of the platinum is separated.—2. Sulphide of platinum precipitated by sulphuretted hydrogen dissolves in aqueous monosulphide of sodium, forming a red solution. (Vauquelin.)

F. Sulphite of Platinous Oxide and Soda.—*a.* $3(NaO,SO^2)+PtO,SO^2$.—1. Formed by precipitating sulphite of platinous oxide with carbonate of soda.—2. By passing sulphurous acid gas through aqueous bichloride of platinum till the liquid is completely saturated, then adding carbonate of soda, and washing the bulky white precipitate with water. In the dry state, it forms a white amorphous powder; in the moist state, it has a tinge of yellow. Remains in the form of a white varnish when the

aqueous solution is evaporated. In the state of aqueous solution, it is neutral to vegetable colours. (Litton & Schnedermann, *Ann. Pharm.* 42, 316.)

| *Dried at* 200°. | | | | Litton & Schnedermann. |
|---|---|---|---|---|
| $3NaO$ | 93·6 | .... 28·48 | .... | 28·14 |
| $PtO$ | 107·0 | .... 32·56 | .... | 31·87 |
| $4SO^2$ | 128·0 | .... 38·96 | .... | 39·24 |
| $3(NaO,SO^2) + PtO,SO^2$ | 328·6 | .... 100·00 | .... | 99·25 |

The salt, after drying at 100°, gives off at 200°, from 4·16 to 4·28 per cent. of water, about $= 1\frac{1}{2}$ At. Above 240°, it becomes darker, and by continued ignition it is completely decomposed, leaving platinum, together with sulphate and sulphite [?] of soda. Chlorine passed through the aqueous solution of the salt exerts a decomposing action. Acids dissolve it with evolution of sulphurous acid; from the solution in hydrochloric acid, ammonia throws down Magnus's green ammonio-protochloride of platinum; the dark sulphuric acid solution contains sulphate of soda and sulphate of platinic oxide, which, when sufficiently concentrated, deposits metallic platinum. The solution of the salt in aqueous cyanide of potassium, deposits, on evaporation, crystals of protocyanide of platinum and potassium. The solution of the salt in water is not precipitated by sulphuretted hydrogen or hydrosulphate of ammonia, excepting on the addition of an acid, which decomposes the salt, and, slowly at ordinary temperatures, but immediately on the application of heat, produces a brown-red colour in the liquid and a deposit of sulphide of platinum. Boiling aqueous hydrosulphate of ammonia or potash gradually dissolves the salt, and an acid added to the solution throws down sulphide of platinum. Boiling solution of potash or soda exerts no decomposing action on the salt. It is but very slightly soluble in cold water, but somewhat more soluble in hot water, so that it becomes turbid on cooling. Common salt throws it down from the solution in white flakes; a similar, but weaker precipitating action is exerted by sal-ammoniac, chloride of barium, and nitrate of silver. The salt is insoluble in solution of common salt and in alcohol. (Litton & Schnedermann.)

*b.* $NaO,SO^2 + PtO,SO^2$.—When the salt (*a*) is dissolved in the smallest possible quantity of dilute sulphuric or hydrochloric acid, and the liquid evaporated at a gentle heat, sulphurous acid is evolved, and a yellowish powder separates, which must be washed with a small quantity of cold water. This salt dissolves in water, with tolerable facility, forming a liquid which reddens litmus slightly, and gives no precipitate with common salt; in other respects it behaves like (*a*). (Litton & Schnedermann.)

| *Dried at* 100°. | | | | Litton & Schnedermann. |
|---|---|---|---|---|
| $NaO$ | 31·2 | .... 14·78 | .... | 15·17 |
| $PtO$ | 107·0 | .... 50·66 | .... | 50·13 |
| $2SO^2$ | 64·0 | .... 30·30 | .... | 30·22 |
| $HO$ | 9·0 | .... 4·26 | | |
| $NaO,SO^2 + PtO,SO^2 + Aq$ | 211·2 | .... 100·00 | | |

G. Sulphate of Platinic Oxide and Soda.—*Basic.*—Obtained like the corresponding potash salt (p. 32). Contains 84·16 per cent. of platinic oxide, 7·11 sulphate of soda, and 8·73 water. (E. Davy.)

H. Iodoplatinate of Sodium.—Formed by dissolving biniodide of

platinum in aqueous iodide of sodium. Lead-grey, striated needles, deliquescent, easily soluble in water and alcohol. (Lassaigne.)

I. Bromoplatinate of Sodium.—Prepared in a similar manner to the potassium-salt. Dark red prisms, permanent in the air, easily soluble in water and alcohol. (Bonsdorff, *Pogg.* 19, 343; 33, 61.)

| *Anhydrous.* | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|
| NaBr | 101·6 | 28·43 | NaBr | 101·6 | 24·70 | 25·55 |
| Pt | 99·0 | 27·70 | Pt | 99·0 | 24·06 | 23·70 |
| 2Br | 156·8 | 43·87 | 2Br | 156·8 | 38·11 | 37·11 |
| | | | 6HO | 54·0 | 13·13 | 13·64 |
| $NaBr,PtBr^2$ | 357·4 | 100·00 | +6Aq. | 411·4 | 100·00 | 100·00 |

K. Chloroplatinite of Sodium.—Prepared like the corresponding potassium-salt.—Red, not crystallizable; easily soluble in water and alcohol. (Magnus.)

L. Chloroplatinate of Sodium.—Aqueous bichloride of platinum mixed with common salt and evaporated, yields the hydrated compound in aurora-red prisms and tables, which, when carefully heated, give off their water, and leave the dry salt in the form of an orange-yellow powder. This powder swells up when more strongly heated, but requires a very high temperature to decompose it completely, being then resolved into a mixture of platinum and chloride of sodium. (Vauquelin.)—The salt dissolves very easily in water and alcohol. Sal-ammoniac added to the aqueous solution throws down chloroplatinate of ammonium, while common salt remains in solution. Potash and soda, either caustic or in the state of carbonate, forms with the solution a precipitate which redissolves in excess of the alkali. (Mussin-Puschkin, *Crell. Ann.* 1800, 1, 91.)

| *Anhydrous.* | | | *Crystallized.* | | | Berzelius. | Vauquelin. |
|---|---|---|---|---|---|---|---|
| NaCl | 58·6 | 25·66 | NaCl | 58·6 | 20.75 | | |
| Pt | 99·0 | 43·35 | Pt | 99·0 | 35·06 | 80·75 | 80 |
| 2Cl | 70·8 | 30·99 | 2Cl | 70·8 | 25·07 | | |
| | | | 6HO | 54·0 | 19·12 | 19·25 | 20 |
| $NaCl,PtCl^2$ | 228·4 | 100·00 | +6Aq. | 282·4 | 100·00 | 100·00 | 100 |

When aqueous bichloride of platinum not containing any free hydrochloric acid is mixed with a quantity of soda not quite sufficient to give it an alkaline reaction, and then left to evaporate spontaneously, brownish yellow and pearly grey laminæ are formed, which are permanent in the air, do not redden litmus, and dissolve readily in water, forming a dark brown solution. These laminæ, when gently heated, turn yellow, and give off 15 per cent. of water; when heated to redness, they leave 20 per cent. of platinum, together with chloride of sodium.

M. Fluoplatinate of Sodium.—Gummy, dark brown; decomposed by contact with water into a soluble acid salt and an insoluble basic salt. (Berzelius.)

N. Nitrate of Platinic Oxide and Soda.—*Basic.*—When solution of platinic nitrate is mixed with soda, pure hydrate of platinic oxide is first precipitated, and afterwards this double salt. Turns white when dry. (Berzelius.)

## Platinum and Barium.

A. Alloy of Platinum and Barium.—Platinum fuses with an equal weight of barium before the oxy-hydrogen blowpipe, forming a bronze-coloured metal, which, in the course of 24 hours, decomposes and leaves a reddish powder. (Clarke, *Gilb.* 62, 372.)

B. Platinate of Baryta.—Precipitated on mixing a platinic salt with a large excess of baryta. Light yellow powder, which, at a red heat, is resolved into a mixture of platinum and baryta. (Berzelius, *Lehrb.*)—The hydrochloric acid solution of platinum behaves with baryta, both in the dark and when exposed to light, just as with lime, and yields a compound perfectly similar to Herschel's precipitate. (Fr. Weiss & Fr. Döbereiner.)

C. Sulphate of Platinic Oxide and Baryta.—Chloride of barium added to a solution of platinic sulphate, produces a brown, tasteless precipitate, which, at a red heat, gives off nothing but water. It is not decomposed by alkalis, dissolves in hot sulphuric acid or aqua-regia, but not in water or in boiling hydrochloric or nitric acid. (E. Davy.)—When chloride of platinum in solution is mixed with chloride of barium and hydrochloric acid added, the whole of the platinic oxide is precipitated together with the sulphate of baryta. (Berzelius, *Ann. Chim. Phys.* 14, 376.)

D. Iodoplatinate of Barium.—Similar to the sodium-salt, but somewhat less deliquescent. (Lassaigne.)

E. Bromoplatinate of Barium.—Red prisms, permanent in dry air. (Bonsdorff.)

F. Chloroplatinate of Barium.—1. A mixture of chloride of platinum and excess of chloride of barium is left to evaporate spontaneously; the resulting crystals dissolved out by a small quantity of cold water, which leaves behind the greater part of the chloride of barium formed at the same time; the solution left to evaporate; the residue again exhausted with cold water, and the solution again evaporated. (Bonsdorff.)—2. Aqueous bichloride of platinum is saturated with baryta-water, or boiled with carbonate of baryta, and the filtrate exposed to the air till it evaporates to the crystallizing point; if baryta-water has been used, the filtrate at first deposits carbonate of baryta. (Berzelius, *Lehrb.*)

Hydrated rhombic prisms, having the angles at their lateral edges equal to 107° and 73°; permanent in the air. (Bonsdorff.) Light yellow (Berzelius); orange-yellow (Bonsdorff). They effloresce at 70°, and leave an opaque powder, which gives off the rest of its water at a higher temperature. When ignited, it leaves platinum together with chloride of barium. (Bonsdorff, *Pogg.* 17, 250.)

| *Anhydrous.* | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|
| BaCl | 104·0 | 37·98 | BaCl | 104·0 | 33·57 | 33·56 |
| Pt | 99·0 | 36·16 | $PtCl^2$ | 169·8 | 54·81 | 52·48 |
| 2Cl | 70·8 | 25·86 | 4HO | 36·0 | 11·62 | 13·96 |
| $BaCl,PtCl^2$ | 273·8 | 100·00 | +4Aq. | 309·8 | 100·00 | 100·00 |

When aqueous bichloride of platinum is boiled with carbonate of baryta, a heavy, orange-yellow powder is precipitated, easily soluble in water: at a red heat, it first gives off water and then decomposes. (Berzelius, *Lehrb.*)

## Platinum and Strontium.

A. Platinate of Strontia.—Similar to platinate of baryta.

B. Chloroplatinate of Strontium.—Prepared like the barium-salt (1). Rhombic prisms, having the angles of their lateral edges about equal to 93° and 87°, and often forming a delicately radiated mass. Permanent in the air, efflorescent in warm air, very easily soluble in water. (Bonsdorff.)

| *Anhydrous.* | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|
| SrCl | 79·4 | 31·86 | SrCl | 79·4 | 24·72 | 24·64 |
| Pt | 99·0 | 39·73 | $PtCl^2$ | 169·8 | 52·86 | 52·52 |
| 2Cl | 70·8 | 28·41 | 8HO | 72·0 | 22·42 | 22·84 |
| $SrCl,PtCl^2$ | 249·2 | 100·00 | +8Aq. | 321·2 | 100·00 | 100·00 |

Carbonate of strontia, like carbonate of baryta, when boiled with aqueous bichloride of platinum, throws down an orange-yellow, pulverulent basic salt. (Berzelius.)

## Platinum and Calcium.

A. Platinate of Lime.—*Herschel's Precipitate.*—Aqueous bichloride of platinum may be mixed in the dark with excess of lime-water, without producing any precipitate. So long as light is excluded, the mixture merely deposits a few flakes after a very long time, and after that, nothing. But in sunshine it becomes milky, and forms an abundant white precipitate, which quickly settles at the bottom. If the quantity of lime is deficient, the precipitate has a pale yellow colour. Violet light acts in the same manner as colourless light, but red or yellow light exerts no action; thus, the mixture remains clear when placed in a tube within a vessel containing sulphuric tincture of roses, or any yellow liquid, and exposed to the sun. (Herschel, *Phil. Mag. J.* 1, 58; also *Schw.* 65, 262; also *Ann. Pharm.* 3, 317.)—The precipitate is yellowish white. (Fr. Döbereiner.)

| $CaCl + CaO,2PtO^2 + 7Aq.$ ? | | | *a.* 1. | *b.* 1. |
|---|---|---|---|---|
| 2Ca | 40·0 | 10·63 | 9·04 | 9·06 |
| 2Pt | 198·0 | 52·60 | 53·02 | 53·70 |
| 5O | 40·0 | 10·63 | 10·45 | 10·49 |
| Cl | 35·4 | 9·40 | 9·37 | 9·35 |
| 7HO | 63·0 | 16·74 | 17·65 | 17·37 |
| | 376·4 | 100·00 | 99·53 | 99·97 |

| | *a.* 2. | *b.* 2. |
|---|---|---|
| CaO | 12·664 | 12·68 |
| Pt | 53·023 | 62·38 |
| O | 8·637 | |
| Cl | 9·368 | 9·35 |
| HO | 17·650 | 17·37 |
| | 101·342 | 101·78 |

*a*, 2; is the original analysis by Fr. Weiss & Fr. Döbereiner (*Ann. Pharm.* 14, 18) of the compound dried at 100° ; *b*, 2, that by Fr. Döbereiner. (*Ann. Pharm.* 14, 252.) In the columns headed *a*, 1, and *b*, 1, the result of these analyses are calculated in such a manner as to be comparable with the preceding theoretical numbers.

The compound, when heated to strong redness in a covered crucible, gives off water and oxygen, together amounting to 25 per cent., and is converted into a dark violet powder, which becomes strongly heated by contact with water, and from which nitric acid dissolves out the lime and chloride of calcium, leaving a residue of dark violet platinous oxide. (W. Döbereiner, *Pogg.* 28, 180.) Hydrochloric acid readily dissolves the compound. Nitric acid dissolves it completely when recently precipitated, but if it be dry, a small quantity of platinic oxide is left. In the resulting solution, nitrate of silver produces an orange-yellow precipitate, insoluble in alkaline hyposulphites. (Herschel.) The compound dissolves in the smallest quantity of nitric acid, and sal-ammoniac added to the solution produces no precipitate for several hours, but the precipitation, when once begun, goes on for several days. (Fr. Weiss & Fr. Döbereiner.)

B. Bromoplatinate of Calcium.—Scarlet prisms permanent in the air. (Bonsdorff.)

C. Chloroplatinate of Calcium.—An aqueous mixture of bichloride of platinum and chloride of calcium, the latter not being in excess, yields, when allowed to evaporate spontaneously, merely dendrites, together with a brownish yellow, gelatinous mass ; but if the mixture contains an excess of chloride of calcium, and is evaporated at a gentle heat, it yields distinct crystals, which may be freed from the deliquescent crystals of chloride of calcium by laying them on blotting-paper. Small, slightly oblique prisms, the terminal faces of which are but little inclined to the adjacent faces ; probably isomorphous with the strontium-salt. When heated, they give off their water of crystallization, and are converted into a yellow powder, which takes up water again when exposed to the air.

| *Anhydrous.* | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|
| CaCl | 55·4 | 24·60 | CaCl | 55·4 | 18·64 | 18·45 |
| Pt | 99·0 | 43·96 | Pt | 99·0 | 33·31 | 32·69 |
| 2Cl | 70·8 | 31·44 | 2Cl | 70·8 | 23·82 | 24·10 |
| | | | 8HO | 72·0 | 24·23 | 24·76 |
| $CaCl,PtCl^2$ | 225·2 | 100·00 | +8Aq. | 297·2 | 100·00 | 100·00 |

## Platinum and Magnesium.

A. Bromoplatinate of Magnesium.—Hydrated deep scarlet prisms, tolerably permanent in the air.

B. Chloroplatinate of Magnesium.—The aqueous solution of the two metallic chlorides yields, on spontaneous evaporation, reddish yellow, six-sided prisms (derived from an acute rhombohedron whose angles are nearly equal to 133°, and needles united in silky tufts ; they are permanent in the air. When heated, they give off 4 atoms of water out of the six, and are reduced to a yellowish brown powder, which, when exposed to the air, soon regains the water which it has lost, recovering at the same

time its former colour, and dissolves in water with evolution of heat. (Bonsdorff.)

| | *Anhydrous.* | | | | *Crystallized.* | | Bonsdorff. |
|---|---|---|---|---|---|---|---|
| MgCl | 47·4 | .... | 21·82 | MgCl | 47·4 | .... 17·48 | .... 18·08 |
| Pt | 99·0 | .... | 45·58 | $PtCl^2$ | 169·8 | .... 62·61 | .... 61·09 |
| 2Cl | 70·8 | .... | 32·60 | 6HO | 54·0 | .... 19·91 | .... 20·83 |
| $MgCl,PtCl^2$ | .... 217·2 | .... | 100·00 | + 6Aq. | .... 271·2 | ....100·00 | .... 100·00 |

When an aqueous solution of bichloride of platinum is boiled with carbonate of magnesia, an orange-yellow powder is produced, which is insoluble in water; and, when heated to redness, leaves a mixture of platinum and magnesia. (Berzelius.)

## Platinum and Aluminum.

Sulphate of Platinic Oxide and Alumina.—Hydrochlorate of alumina added to a solution of platinic sulphate, produces a brown, gelatinous precipitate, which dries up to a black, shining powder, permanent in the air. This powder, when heated to redness, gives up nothing but water, amounting to 27 per cent.; it is insoluble in water and in cold mineral acids, very slightly soluble in hot acids. (E. Davy.)

## Platinum and Silicium.

A. Silicide of Platinum.—1. Silicium ignited by itself in a platinum crucible, does not combine with its substance; but when silicofluoride of potassium is reduced by potassium, the silicium penetrates deeply into the crucible at the points in which the potassium touches the sides. (Berzelius, *Pogg.* 1, 220.)—2. Platinum fuses when covered with charcoal powder and exposed to the heat of a powerful forge, taking up at the same time $\frac{1}{2}$ p. c. of silicium; but when covered with lamp-black, which does not contain silica, it exhibits no signs of fusion. (Boussingault, Berzelius.)—3. Platinum foil immersed in charcoal-powder, and exposed for four hours to the heat of a blast-furnace not strong enough to fuse it, is likewise penetrated by silicium and loses its lustre. (Boussingault.) The compound of silicium and platinum is greyish white, hard, of granular fracture, difficult to cut or file; scratches platinum and iron, and does not become harder by rapid cooling; (2) has a specific gravity of 20·5 (Boussingault); 18·3 (Berzelius); (3) has a sp. gr. varying from 17·5 to 18·0. (Boussingault.) When cold, it soon splits under the hammer; at a red heat, it is perfectly brittle. Its ductility is not restored either by heating it in contact with the air, or by cementation with peroxide of manganese. Dissolves in aqua-regia less easily than platinum, and with separation of a thick crust of gelatinous silica, which, when completely separated by evaporation and digestion in water, amounts to 1 per cent. (Boussingault, *Ann. Chim. Phys.* 16, 5.) The properties of this compound account for the fact that Prechtl (*Gilb.* 58, 112) found platinum fusible in the heat of a powerful blast-furnace, but obtained a button which had a sp. gr. of 17·7, and was not malleable, especially when hot.

B. Platinic Silico-fluoride. — The yellow solution of hydrated platinic oxide in hydrofluosilicic acid dries up to a yellowish brown gum,

which, when redissolved in water, leaves a brown *basic salt.* (Berzelius, *Pogg.* 1, 201.)

C. The platinous oxide obtained by E. Davy (p. 282) forms a dark brown vitreous mass, when fused with pounded glass.

¶ A mixture of 1 pt. pulverized spongy platinum (prepared from chloroplatinate of ammonium) and 3 parts of a flux composed of 3 pts. minium, 1 pt. sand, and ½ pt. fused borax, is used at Sèvres for producing a grey colour on porcelain. (Salvétat, *N. Ann. Chim. Phys.* 25, 342.)¶

## Platinum and Tungsten.

A. Alloy of Platinum and Tungsten.—Brittle and easily pulverized. (De Luyart.)

B. Platinic Sulphotungstate. — $PtS^2,2WS^3$. — Aqueous sulphotungstate of potassium forms with platinic salts a deep red liquid, which, after some time, deposits a black precipitate. (Berzelius.)

## Platinum and Molybdenum.

A. Alloy of Platinum and Molybdenum.—Equal portions of the two metals yield a hard, brittle, shapeless lump, which appears compact on the fractured surface ; it has a light grey colour and metallic lustre, 4 pts. of platinum with 1 pt. of molybdenum form a hard, brittle, bluish grey alloy, having a granular fracture. (Hgelm.)

B. Platinic Sulphomolybdate.—$PtS^2,2MoS^3$.—Black-brown precipitate. (Berzelius.)

C. Platinic Persulphomolybdate.—Dark red precipitate. (Berzelius, *Pogg.* 7, 286.)

## Platinum and Vanadium.

Alloy of Platinum and Vanadium.—A platinum crucible in which preparations of vanadium have frequently been ignited, becomes covered with a thin film of this alloy, but without alteration of colour or lustre ; on ignition in contact with air, it acquires a coating of fused vanadic acid, which prevents the further oxidation of the alloyed vanadium. To clean the crucible, it is therefore necessary to remove the vanadic acid by potash, again ignite it in the air, once more treat it with potash, and repeat these operations 5 or 6 times.

## Platinum and Chromium.

Chromate of Platinic Oxide.—Chromate of potash added to aqueous bichloride of platinum, produces a deep red precipitate, which assumes a brick-red colour on drying. (Thomson.)

## Platinum and Manganese.

A. Bromoplatinate of Manganese.—Dark red, six-sided prisms, which appear to be isomorphous with the magnesium-salt; they are permanent in tolerably dry air, but deliquesce in a damp atmosphere. (Bonsdorff.)

B. Chloroplatinate of Manganese.—Prepared like the magnesium salt, and similar to it in crystalline form. Colour, deeper yellow. When the water of crystallization is driven off, the salt crumbles to a pale lemon-yellow powder. (Bonsdorff.)

| | *Anhydrous.* | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|
| MnCl | 63·4 | .... | 27·19 | MnCl | 63·4 | .... 22·08 | .... 23·02 |
| Pt | 99·0 | .... | 42·45 | $PtCl^2$ | 169·8 | .... 59·12 | .... 58·63 |
| 2Cl | 70·8 | .... | 30·36 | 6HO | 54·0 | .... 18·80 | .... 18·35 |
| $MnCl,PtCl^2$ | 233·2 | .... | 100·00 | +6Aq. | 287·2 | .... 100·00 | .... 100·00 |

## Platinum and Arsenic.

A. Arsenide of Platinum.—100 parts of spongy platinum heated with excess of arsenic, yield 173·5 parts of arsenide of platinum, the combination being attended with vivid combustion. When platinum is heated with arsenious acid and carbonate of soda, arsenide of platinum and arseniate of soda are formed. Arsenious or arsenic acid heated with platinum, without the addition of carbonate of soda, exerts no action on the metal. (Gehlen.)—Arsenic wrapped up in platinum foil, likewise exhibits vivid combustion before the blowpipe. (Murray, *Edinb. Phil. J.* 4, 202.)—The alloy is brittle, and easily fusible. When it is heated in the air for some time, at a continually increasing temperature, but not sufficient to melt it, the arsenic gradually burns away, and leaves a porous residue of platinum in a state fit for working.

B. Arseniate of Platinic Oxide, or Platinic Arseniate.—Arseniate of soda mixed with platinic nitrate, forms a light brown precipitate, soluble in nitric acid. (Thomson.)

C. Platinic Sulpharsenite.—The precipitate, which is of a deep yellow colour at first, gradually becomes dark brown, and black after drying; its powder is dark brown. When subjected to distillation, it gives off part of its orpiment, then fuses, and solidifies on cooling in a black mass, having a vitreous fracture, and yielding a grey metallic powder; at a white heat, the compound gives off more orpiment, and shrinks up to a lighter coloured porous lump, which still contains sulphur and arsenic, and fuses readily before the blowpipe.

D. Platinic Sulpharseniate.—Both terbasic and bibasic sulpharseniate of sodium form, with aqueous bichloride of platinum, a deep yellow liquid, which gradually acquires a dark brown colour, and is decolorized by green vitriol, with precipitation of a brown-black substance.

Bichloride of platinum mixed with aqueous arsenious acid, and then with a small quantity of ammonia, forms a yellow precipitate, which

soon changes to green, and when heated yields a sublimate of sal-ammoniac and arsenious acid, and leaves metallic platinum.

### Platinum and Antimony.

Antimonide of Platinum. — 1 part of spongy platinum unites easily with 2 parts of pulverized antimony, the combination being attended with vivid incandescence; and when the temperature is further raised, the compound fuses into a steel-grey, brittle, fine-grained alloy. (Gehlen.) Vivid incandescence is likewise produced by wrapping antimony in thin platinum foil, and heating it before the blowpipe. (Murray.)—The alloy when heated in the air, gives up its antimony almost wholly, and leaves malleable platinum. (Fox, *Ann. Phil.* 13, 467.)

### Platinum and Tellurium.

Platinic Sulphotellurite.—$3PtS^2,2TeS^2$.—Sulphotellurite of potassium forms, with aqueous bichloride of platinum, a dark yellow mixture, which, after a few days, deposits the sulphur-salt in dark blue flakes, black after drying. (Berzelius.)

### Platinum and Bismuth.

Alloy of Platinum and Bismuth.—1 part of spongy platinum and 2 parts of bismuth heated together, combine readily, but without visible combustion, and form a bluish grey, brittle, easily fusible alloy, having a laminated fracture. (Gehlen.) When this alloy is fused at a moderate heat, the two metals separate partially, according to their densities. When it is strongly ignited in contact with air, the greater part of the bismuth burns and forms a vitreous oxide, till the residue is no longer fusible.

### Platinum and Zinc.

A. Alloy of Platinum and Zinc.—1 part of spongy platinum combines with $1\frac{1}{2}$ to 2 parts of zinc, at a temperature below redness, producing vivid combustion, sometimes amounting to explosion. (Gehlen, Fox). Zinc wrapped up in platinum foil, and heated before the blowpipe, produces more vivid combustion than any other metal under similar circumstances. (Murray.)—The compound is bluish white, very hard, and easily fusible. Platinum is rendered brittle by admixture with $\frac{1}{4}$ pt. of zinc, and zinc by $\frac{1}{20}$ pt. of platinum. The alloy, when ignited in the air, loses the greater part of its zinc by oxidation, and at length becomes infusible.

The black powder which remains, on treating the alloy of 1 pt. platinum and 4 pts. zinc with dilute sulphuric acid, is not pure platinum, but contains 31 per cent. of zinc; it gains 3 per cent. by ignition in the air. (Boussingault, *Ann. Chim. Phys.* 53, 444.)

B. Iodoplatinate of Zinc.—Imperfectly crystallized, deliquescent, saline mass, having an astringent taste. (Lassaigne.)

C. Bromoplatinate of Zinc.—Deep red, six-sided prisms, terminated with the faces of a rhombohedron, and needles united in tufts; permanent in the air. They are isomorphous with the following chlorine compound E, and with the corresponding bromine and chlorine salts of magnesium and manganese. (Bonsdorff.)

D. Chloroplatinite of Zinc.—Obtained by partially precipitating the solution of platinum in excess of aqua-regia with zinc, continuing the action till the solution acquires a paler yellow colour, and evaporating the filtrate. Crystals of D are first produced and afterwards of E. If the zinc acts for a short time only, the resulting crystals consist principally of E; but if the action be continued, till a yellowish powder is precipitated together with the platinum, and the liquid be then well boiled and filtered, the chief product obtained is D. Small, shining, light yellow, tolerably hard crystals. When heated in a glass tube, they assume a dark orange, and afterwards a brownish yellow tint, without giving off water; at a higher temperature, they are resolved, with transient jumping motion, into chlorine, platinum, and chloride of zinc. They are but slightly attacked by sulphuric acid. They are very sparingly soluble in cold water, more easily in boiling water, and are separated from the solution by cooling or by the addition of alcohol. The aqueous solution forms a brown precipitate with hydrosulphate of ammonia, a beautiful yellow precipitate with the hydrochloric acid solution of dichloride of copper, and a dingy flesh-coloured precipitate with nitrate of silver. (Hünefeld, *Schw.* 60, 197.)

| | | | | Or: | | | | Hünefeld. |
|---|---|---|---|---|---|---|---|---|
| ZnCl | 67·4 | .... | 33·40 | Zn | 32·0 | .... | 15·86 | .... 16·0 |
| Pt | 99·0 | .... | 49·06 | Pt | 99·0 | .... | 49·06 | .... 47·8 |
| Cl | 35·4 | .... | 17·54 | 2Cl | 70·8 | .... | 35·08 | .... 34·6 |
| ZnCl,PtCl | 201·8 | .... | 100·00 | | 201·8 | .... | 100·00 | .... 98·4 |

E. Chloroplatinate of Zinc.—1. Prepared by the same process as D, the action of the zinc being continued for a shorter time only. The salt D which crystallizes out at first, is separated from E, which separates later, by digestion in alcohol, which dissolves the salt E. (Hünefeld.)—2. Concentrated solutions of bichloride of platinum and chloride of zinc become very hot when mixed, and the mixture immediately deposits crystals of the double chloride. (Bonsdorff.)

Large orange-yellow prisms, of the form of zircon; they yield an orange-yellow powder, and have an astringent taste. (Hünefeld.) They are isomorphous with the corresponding salts of magnesium and manganese. (Bonsdorff.) The crystals, when heated, give off water and turn brown, afterwards grey, and at a red heat, yield chlorine gas and sublimed chloride of zinc, leaving a residue of platinum. Sulphuric acid decomposes them readily, with evolution of hydrochloric acid and chlorine. They deliquesce in the air (Bonsdorff asserts the contrary), and are easily soluble in water and alcohol. The aqueous solution gives a brown precipitate with hydrosulphate of ammonia, and yellow with the hydrochloric acid solution of dichloride of copper, and with nitrate of silver. (Hünefeld.)

| | *Anhydrous.* | | | *Crystallized.* | | | | Hünefeld. |
|---|---|---|---|---|---|---|---|---|
| ZnCl | 67·4 | .... | 28·41 | Zn | 32·0 | .... | 10·99 | .... 10·76 |
| Pt | 99·0 | .... | 41·74 | Pt | 99·0 | .... | 34·00 | .... 33·34 |
| 2Cl | 70·8 | .... | 29·85 | 3Cl | 106·2 | .... | 36·47 | .... 35·26 |
| | | | | 6HO | 54·0 | .... | 18·54 | |
| $ZnCl,PtCl^2$ | 237·2 | .... | 100·00 | +6Aq. | 291·2 | .... | 100·00 | |

## Platinum and Cadmium.

A. Alloy of Platinum and Cadmium.—Formed by heating platinum with excess of cadmium, till the excess is volatilized. Almost silver-white, very brittle, very fine-grained, and refractory in the fire. Contains 46·02 (1 At.) platinum and 53·98 (2 At.) cadmium. (Stromeyer.)

B. Chloroplatinate of Cadmium.—The hydrated crystals have the same form as those of the magnesium-salt, and are prepared in a similar manner; they are of a deeper yellow colour than the magnesium-salt. (Bonsdorff.)

## Platinum and Tin.

A. Alloy of Platinum and Tin.—1 part of spongy platinum and 2 parts of tin-filings heated together, become bright red-hot and yield a tin-white, brittle alloy having a laminated texture. (Gehlen.) When tin-foil is rolled up with fine platinum foil and heated before the blowpipe on charcoal, combination takes place, attended with a kind of explosion. (Clarke, *Ann. Phil.* 14, 329 and 470; Murray, *Edinb. Phil. J.* 4, 202.) Equal parts of the two metals form a dark-coloured, hard, brittle, tolerably fusible alloy, having a coarse granular structure. The alloy of 12 pts. tin and 1 platinum is somewhat malleable.

The precipitate formed in solution of bichloride of platinum by protochloride of tin, is probably a compound of stannic acid and protoxide of platinum.

B. Stannous Chloroplatinite.—*a. With a comparatively large proportion of tin.*—Deep red. Dissolves but sparingly in water, producing a bright red solution; a larger quantity decomposes it into hydrochloric acid and a chocolate-coloured powder, which contains stannous oxide as well as stannous chloroplatinite, yields black crystalline grains when ammonia is poured upon it, and burns away like tinder, when heated, leaving stannic oxide and platinum. (Kane.)—*b. With a smaller quantity of tin.*—Greenish brown, crystalline, very deliquescent; decomposed by a large quantity of water into stannic oxide and platinic oxide [platinous?]. (Kane, *Phil. Mag. J.* 7, 399; also *J. pr. Chem.* 7, 135.)

## Platinum and Lead.

Alloy of Platinum and Lead.—Melted lead poured into a platinum crucible dissolves a portion of the platinum. (Berzelius.) Lead wrapped in platinum foil exhibits incandescence when heated. (Murray.)—1 part of spongy platinum and 2·7 of lead heated to redness together, combine without visible combustion and form an easily fusible compound, which has the colour of bismuth, splits under the hammer, and exhibits a fibrous fracture. The alloy of 1 pt. platinum and 2 pts. lead is somewhat more brittle. (Gehlen.) An alloy containing equal quantities of the two metals has a purple colour and striated surface, and is hard, brittle, exhibits a granular fracture, and is altered by exposure to the air. When these alloys are heated to redness in the air, only part of the lead separates from the platinum, the separation going on indeed only so long as the alloy remains fusible.

## Platinum and Iron.

A. Alloy of Platinum and Iron.—Equal weights of platinum and iron heated before the oxy-hydrogen blowpipe unite, with vivid emission of sparks, and form a shining, very hard and malleable alloy, which is scarcely touched by the file. In equal volumes, the two metals yield a brittle button. (Clarke.) Combination does not take place in the heat of an ordinary fire. (Lewis, Gehlen.) An alloy of 99 pts. iron and 1 pt. platinum is not attacked by ordinary nitric acid. (Schönbein, *Pogg.* 42, 17.)

When equal weights of iron and platinum are dissolved in aqua-regia, the excess of acid expelled by evaporation, the solution precipitated by ammonia, and the washed precipitate reduced in a stream of hydrogen at a low red heat, an alloy of iron and platinum is obtained, which immediately takes fire on exposure to the air. If this alloy, without being allowed to come in contact with air, so that no combustion may take place, be thrown into hydrochloric acid—which dissolves part of the iron, with evolution of hydrogen,—and the residue washed with water, there remains a black heavy powder, containing 80·1 p. c. platinum to 19·9 iron (which may be dissolved out by boiling nitric acid) together with a trace of moisture, but no hydrogen. This residue takes fire in the air considerably below a red heat, and burns with emission of sparks. Sometimes the combustion begins at the hottest part and spreads through the mass with a red light, as in the burning of tinder; after the combustion, the powder is found to have gained 1 per cent. in weight. (Boussingault, *Ann. Chim. Phys.* 53, 441.)

B. Carbide of Platinum and Iron.—*a. With Steel.*—*α.* 9 pts. platinum with 2 pts. steel. Perfect alloy which does not tarnish on exposure to the air; sp. gr. 15·88.—*β.* 1 pt. platinum to 1 pt. steel. Takes a high polish, does not tarnish, exhibits a highly crystalline structure on the surface, and has a density of 9·862.—*γ.* 1 pt. platinum to 8 pts. steel. Finely damasked alloy.—*δ.* 1 platinum to 10 steel; sp. gr. 8·1.—*ε.* 1 pt. platinum to 67 pts. steel. The best adapted for cutting instruments.—*ζ.* 1 pt. platinum to 100 pts. steel. Of uniform surface, and beautiful fracture; not so hard as silver-steel, but much tougher, and therefore specially adapted to many purposes. (Faraday & Stodart, *Gilb.* 66, 196; 72, 225.)—*η.* 1 pt. platinum to 200 steel. Damasked alloy, very well adapted for razors. (Bréant.) Steel alloyed with a small quantity of platinum dissolves in dilute sulphuric acid much more quickly than pure steel. This increase of solubility is produced even by $\frac{1}{400}$ pt. of platinum, and is strongest with a quantity between $\frac{1}{200}$ and $\frac{1}{100}$. With $\frac{1}{40}$ of platinum, the solubility is perceptibly less; steel alloyed with one-half platinum does not dissolve more quickly than pure steel; and a compound of 2 parts steel with 9 platinum is not at all affected by dilute sulphuric acid. These alloys exhibit the same relations towards other dilute acids. (Faraday & Stodart, *Ann. Chim. Phys.* 21, 67; *comp.* V, 210.)

When a compound of 100 parts of steel with 1 part of platinum (or of any other metal insoluble in nitric acid) is treated with dilute sulphuric acid, and the undissolved portion, containing platinum, iron, carbon, and hydrogen, is boiled with nitric acid, a black residue is left. This latter substance, when heated to 200°, detonates slightly, producing a faint

light, but if gradually heated, decomposes without detonation; it dissolves in aqua-regia, yielding a solution containing a large proportion of platinum with but little iron. (Faraday & Stodart.)

*b. With Cast-iron*, platinum forms a dark, malleable, and very hard alloy. (Lewis.)

C. Ferrous Iodoplatinate.—The blood-red solution of biniodide of platinum in aqueous protiodide of iron, leaves, when evaporated in vacuo, a non-crystalline, deliquescent mass. The aqueous solution, when exposed to the air, deposits ferric oxide, and is converted into a carmine-coloured solution of biniodide of platinum in sesquichloride of iron. (Lassaigne.)

D. Ferrous Chloroplatinate.—Preparation and crystalline form of the hydrated salt, the same as of the corresponding magnesium-salt; the evaporation is best performed under a bell-jar not exhausted of air. The dark yellow crystals become covered, on exposure to the air, with a red-brown powder, and their aqueous solution deposits the same substance when left in an open vessel. (Bonsdorff.)

| | *Anhydrous.* | | | *Crystallized.* | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|
| FeCl | 63·4 | 27·19 | FeCl | 63·4 | 22·08 | | 21·32 |
| Pt | 99·0 | 42·45 | $PtCl^2$ | 169·8 | 59·12 | | 60·45 |
| 2Cl | 70·8 | 30·36 | 6HO | 54·0 | 18·80 | | 18·23 |
| $FeCl,PtCl^2$ | 233·2 | 100·00 | +6Aq. | 287·2 | 100·00 | | 100·00 |

## Platinum and Cobalt.

Chloroplatinate of Cobalt.—Preparation and crystalline form, as with the magnesium-salt; colour, a somewhat deeper yellow. (Bonsdorff.)

## Platinum and Nickel.

A. Alloy of Platinum and Nickel.—Equal parts of these metals placed upon a piece of charcoal burning in a stream of oxygen, unite quickly, and form a pale yellowish white alloy, perfectly malleable, susceptible of a high polish, equal to copper in fusibility and to nickel in magnetic power. (Lampadius.)

B. Chloroplatinate of Nickel.—Preparation and crystalline form of the hydrated salt, as with the magnesium-salt. Colour, greenish yellow. (Bonsdorff.)

## Platinum and Copper.

A. Alloy of Platinum and Copper.—Combination does not take place below a white heat.—Equal weights of platinum and copper, heated together in the oxy-hydrogen blowpipe flame, yield a pale yellow alloy having the colour and specific gravity of gold, extensible, easily attacked by the file, and tarnished by exposure to the air. (Clarke.)—An alloy of 26 parts copper and 1 platinum, is malleable, rose-coloured, and exhibits a fine-grained fracture.

B. Chloroplatinate of Copper.—Preparation and crystalline form

of the hydrated salt, as with the magnesium-salt. The pale olive-green crystals are best obtained by evaporation over oil of vitriol in a chamber not exhausted of air; but if kept too long there, they effloresce and become greenish grey. They are permanent in a warmed winter atmosphere, but deliquesce in a summer atmosphere. (Bonsdorff.)

C. Alloy of Platinum, Copper, and Zinc.—7 pts. of platinum fused at a white heat with 16 parts of copper, under a covering of borax and charcoal, and then, after the crucible has been removed from the fire, united by agitation with 1 part of zinc, yield a gold-coloured, highly extensible alloy, which does not oxidate by roasting and is not attacked by boiling sulphuric acid. (Cooper.) A mere trace of iron renders it less malleable.—*Other directions:* 1 pt. platinum, 6 copper, 1 brass, and 1 zinc; or, 2 pts. platinum, 2 silver, 12 copper, 1 brass, 1 zinc. (Burle, *J. Chim. méd.* 8, 557.)

## Platinum and Mercury.

Amalgam of Platinum.—Hammered platinum does not take up mercury at ordinary temperatures, though kept in contact with it for six years; if heated, however, it becomes covered with a film of mercury which may easily be wiped off. (Daniell.)—1. The amalgam may be obtained by triturating spongy platinum with mercury. Böttger uses a warmed mortar for this purpose; Daniell accelerates the amalgamation by adding water during trituration, water containing acetic acid being best adapted for the purpose.—2. By immersing sodium-amalgam (containing $\frac{1}{100}$ sodium) in a concentrated aqueous solution of bichloride of platinum. Hydrogen gas is then given off in abundance, and, if the liquid be too much concentrated, pure platinum separates in the form of a soft, black powder. (Böttger.)—3. By triturating 2 measures of platinum sal-ammoniac, made up into a paste with water, with about one measure of sodium-amalgam. The platinum sal-ammonic turns black, and gives off ammonia [and hydrogen] with a hissing noise; when the evolution of gas ceases, the formation of the amalgam is complete; it may be washed with water by decantation. (Böttger.)—The amalgam obtained by (1) is solid, if the platinum is in excess, but of an unctuous consistence when it contains excess of mercury. At a strong red heat, the mercury goes off, and the platinum remains in a finely-divided and porous state (Daniell, *Schw.* 33, 100); but if pressure has been applied during the ignition, the residual platinum is fit for working. (Mussin-Puschkin, *A. Gehl.* 3, 453.) This amalgam may be used for covering copper, silver, and gold with platinum. (*Gilb.* 24, 402.)

When the amalgam obtained by (2) or (3), which has the appearance of a viscid paste, is heated in a watch-glass by the flame of a common spirit-lamp, it boils up and leaves a grey, coherent mass; and this, when pulverized after cooling and again ignited over the alcohol flame, leaves a dull black powder, which even after heating for a considerable time, still retains $\frac{1}{13}$ of mercury. The residue, boiled for several hours with strong nitric acid (which extracts but a trace of mercury from it even in 24 hours), then washed with water, and dried, exhibits in a high degree the inflaming power of platinum on hydrogen gas and alcohol, notwithstanding that it contains mercury. At a still higher temperature, the mercury goes off, leaving grey, coherent platinum, which no longer sets

fire to hydrogen. The black powder is insoluble in cold, but soluble in warm aqua-regia. If the platinum-amalgam, instead of being heated, be immediately digested with nitric acid frequently renewed, there remains a black powder mixed with a few shining particles of platinum, which does not set fire to a mixture of hydrogen and air at ordinary temperatures, but when heated in that mixture, becomes red hot, sets fire to the gas, and is converted into spongy platinum. (Böttger, *J. pr. Chem.* 3, 278.)

Calomel dissolves in a hot aqueous solution of bichloride of platinum, and the liquid, on cooling, deposits crystals, which have not been further examined. (Bonsdorff, *Pogg.* 19, 353.)—Mercurous nitrate forms with aqueous bichloride of platinum a brown, pulverulent precipitate, which, when gently heated, yields a sublimate of calomel and leaves protoxide of platinum. (Berzelius, *Lehrbuch.*)

## Platinum and Silver.

Alloy of Platinum and Silver.—Silver, by combination with platinum, becomes less white, less malleable and harder; when the alloy is quietly fused, a compound richer in platinum collects at the bottom. Hot oil of vitriol dissolves out the silver and leaves the platinum. (D'Arcet.) Nitric acid always dissolves a small quantity of platinum together with the silver.

When aqueous bichloride of platinum, made as neutral as possible, is mixed with nitrate of silver, the liquid becomes decolorized, and a yellow precipitate is formed, which appears to be a compound of chloride of silver with basic hydrochlorate of platinic oxide [or bichloride of platinum?]; this precipitate gives off chlorine at a red heat, leaving platinum together with chloride of silver, and when treated with hydrochloric acid, gives off all its platinum, and leaves chloride of silver. (Vauquelin.) The precipitate is curdy and yellow, becoming dirty white when washed. Ammonia dissolves out only part of the chloride of silver, leaving a yellow mixture of platinum sal-ammoniac and chloride of silver, from which boiling water first extracts pure platinum sal-ammoniac, afterwards the same compound mixed with a little chloride of silver; after ignition, it gives up all its chloride of silver to ammonia. (Herberger, *Repert.* 55, 210.)

## Platinum and Gold.

Alloy of Platinum and Gold.—*a.* 7 pts. platinum to 3 gold. Infusible in the strongest blast-furnace. Alloys containing a larger proportion of gold fuse at that degree of heat. (Prinsep.)—*b.* 2 pts. platinum to 1 gold: brittle. (Clarke.)—*c.* 1 pt. platinum to 1 gold: very malleable; has nearly the same colour as gold. (Clarke.)—*d.* 1 pt. platinum to 9·6 gold: has the colour of gold and the density of platinum. (Clarke, *Gilb.* 68, 269.)—*e.* 1 pt. platinum to 11 gold: greyish white, like tarnished silver. (Hatchett.)

Platinum likewise combines with *Palladium.*

## Chapter XL.

# PALLADIUM.

*Besides the Memoirs cited on p. 252:*

Wollaston. *Phil. Trans.* 1804, 419; also *A. Gehl.* 5, 175.—*Phil. Trans.* 1805, 316; also *N. Gehl.* 1, 231.
Chenevix. *Phil. Trans.* 1803, 4; also *A. Gehl.* 1, 174.
Vauquelin. *Ann. Chim.* 88, 167; also *Schw.* 12, 265; also *A. Tr.* 24, 1, 273.
Berzelius. *Schw.* 7, 66.—*Pogg.* 13, 454.
Fischer. *Schw.* 51, 192.—Further, *Pogg.* 71, 431; abstr. *Ann. Pharm.* 64, 260.

*History.* Palladium was discovered and investigated by Wollaston in 1803. The statement of Chenevix, that it was a compound of platinum and mercury, was shown to be incorrect by Val. Rose & Gehlen (*A. Gehl.* 1, 529), by Trommsdorff (*A. Gehl.* 2, 238), and by Wollaston. Berzelius discovered the oxide and many other compounds of palladium.

*Sources.* 1. Single grains of pure palladium are found mixed with the grains of platinum ore from Brazil. (Wollaston, *Phil. Trans.* 1809, 1, 89; also *Gilb.* 36, 303.) Native palladium, mixed with gold and selenide of lead, is likewise found at Tilkerode; it was at first taken for selenide of platinum. (Bennecke, Rienecker, & Zinken, *Pogg.* 16, 491; G. Rose, *Pogg.* 55, 329.)—2. In the platinum ore from South America (amounting to $\frac{1}{200}$ in the Peruvian ore: *Wollaston*), from Domingo (*Schw.* 1, 364), and from the Ural (p. 254).—3. In combination with gold in an auriferous sand from Zacotinga and Condonga in Brazil, which is mixed with specular iron ore. (Cloud, *Gilb.* 36, 310; also *Schw.* 1, 370; Johnson & Lampadius, *J. pr. Chem.* 11, 309.) The palladium in this ore amounts to 5 or 6 per cent. (Cock.)—4. In combination with a large quantity of gold and a small quantity of silver, in the ore called *Oro pudre* from Porpez in South America; it amounts to 10 per cent. (Berzelius, *Pogg.* 35, 514.)

*Preparation.* 1. From platinum ore: (p. 256, Nos. 3 and 9; p. 257, No. 14; p. 261, No. 16; p. 264, Nos. 14–16; p. 267, No. 8).

2. From the palladiferous gold of Brazil. The gold-dust is fused with an equal weight of silver and a certain quantity of nitre, whereby the earthy matters and the greater part of the base metals are removed in the form of slag; the alloy is then cast in the form of bars; the latter again fused in a black-lead crucible, stirring constantly with an equal weight of silver, so that the gold amounts to about one-fourth of the whole mixture. The alloy is then very finely granulated by pouring it through an iron

sieve into water; the granules heated in a porcelain basin with an equal quantity of nitric acid and an equal quantity of water, as long as any action goes on; the liquid decanted, and the residual gold boiled for two hours with a quantity of pure nitric acid equal to two-thirds of the granules used, after which it is washed with hot water, dried, and fused into a button. From the resulting nitric acid solutions, the silver is precipitated by common salt. The remaining liquid being put into wooden vessels, the palladium and copper are precipitated by zinc; the black powder dissolved in nitric acid; the solution supersaturated with ammonia, which generally leaves undissolved a small quantity of platinum, iron, and lead; and the filtrate containing the palladium and copper, very slightly supersaturated with hydrochloric acid, whereby the greater part of the palladium is precipitated in the form of yellow ammonio-protochloride, which is then washed with cold water and converted into pure palladium by ignition. The remainder of the palladium and the whole of the copper may be precipitated from the hydrochloric acid solution by iron. (Johnson, *J. pr. Chem.* 11, 309; Cock, *Phil. Mag. J.* 23, 16; also *Ann. Pharm.* 49, 236; also *J. pr. Chem.* 30, 20.)

By igniting the cyanide or the ammonio-protochloride of palladium, the metal is obtained in the form of a grey spongy mass. To render it malleable, it must either be fused in the oxygen gas blowpipe, or welded in the following manner: The metal is fused with sulphur—the sulphide of palladium melted in an open crucible with borax and a small quantity of nitre, in order to clean it—then taken out of the crucible, placed upon a brick, and exposed to a low red heat, whereby it acquires the consistence of dough, and may be reduced by pressure to a flat, four-sided, or oval cake. The roasting, which is attended with a slow evolution of sulphur in the form of sulphurous acid, is continued at a low red heat, till the cake becomes spongy on the surface,—after which it is left to cool thoroughly and then beaten with a light hammer, to give it compactness, and remove the spongy growths. It is then again roasted for a considerable time, once more gently hammered after cooling, and the same treatment again repeated. The operation requires the greatest care and patience, because the cake will not at first bear heavy blows. The hammering at length renders it flat and solid enough to be passed between rollers and reduced to leaf of any required degree of thinness. But it always remains somewhat brittle, especially at a high temperature, probably because it retains a small quantity of sulphur. (Wollaston, *Schw.* 57, 81; also *Pogg.* 16, 166.) Palladium may also be rendered malleable by the process which Wollaston applies to platinum (p. 271), but it never becomes so ductile as platinum.

*Properties.* Crystallizes in six-sided tables, with distinct cleavage parallel to the terminal faces. (G. Rose.) The crystals are white, with a strong lustre, of almost microscopic size, and attached to laminæ of native gold. (G. Rose.) The native palladium from Brazil exhibits a fibrous structure, and may be thereby distinguished and separated from the grains of platinum with which it is mixed. (Wollaston.) Specific gravity of fused palladium, 11·04 at 18° (Cloud), 11·3 (Cock), from 11·3 to 11·8 (Wollaston); of hammered palladium, 11·8 (Cock), 11·852 (Lampadius), rather more than 12·0 (Vauquelin), 12·148 (Lowry). Ductile, but somewhat less so than platinum; may be rolled out into thin leaves. Palladium prepared from the sulphide (*vid. sup.*) is ductile when cold, somewhat brittle at a high temperature (Wollaston); that which has been rendered

compact by the same method as platinum, is apt to crack at the edges when hammered cold. (Biewend, *J. p. Chem.* 23, 248.) Palladium is as hard as platinum. It likewise resembles that metal in colour and lustre, but is somewhat darker. Finely-divided palladium, floating in water, exhibits a blood-red colour by transmitted light. (Biewend.) Palladium does not fuse, even at the heat of a very powerful blast-furnace; but its particles adhere together sufficiently to allow the mass to be afterwards hammered and rolled. (Vauquelin, Cock.) In an iron-assay furnace it exhibits incipient fusion. (Biewend.) It fuses about as easily as bar-iron. (Bréant.) Melts and boils when heated on a piece of charcoal ignited in a stream of oxygen. (Vauquelin.)

## *Compounds of Palladium.*

### Palladium and Oxygen.

### A. Protoxide of Palladium, or Palladious Oxide.

Formerly called *Palladic Oxide, Palladiumoxyd.* — *Formation.* — Bright metallic palladium assumes a violet tint when heated to dull redness in the air, and if the heat be longer continued, acquires a blue tarnish; at higher temperatures, however, it recovers its metallic lustre, and retains it if afterwards suddenly cooled, *e.g.* by immersion in water. (Bréant.) Palladium obtained in the finely-divided state by reducing the chloropalladite of potassium with hydrogen gas, becomes covered with a fine blue film on exposure to the air, but does not receive any accession of weight which can be detected by the balance; the blue colouring is removed by hydrogen gas. (Berzelius.) Palladium exposed for some time to a low red heat, becomes covered with a friable crust of brown protoxide, which however is reduced at a higher temperature. (Cock.) When heated to its boiling point on charcoal burning in a jet of oxygen, or before the oxy-hydrogen blowpipe, the metal burns, with emission of bright red sparks. (Vauquelin, Clarke, *Ann. Phil.* 17, 424.)—2. The metal is oxidized and dissolved by nitric acid and aqua-regia at ordinary temperatures, and slowly by boiling oil of vitriol. Palladium dissolves much less quickly in pure nitric acid than in that which contains nitrous acid. (Wollaston.) Pure palladium dissolves but slowly in nitric acid; when alloyed with copper or silver, it dissolves easily. The black powder obtained by precipitating a solution of palladium and copper with zinc dissolves very easily in nitric acid, and even in heated hydrochloric or sulphuric acid. (Cock.)—3. When ignited with hydrate of potash and nitre, it is converted into protoxide of palladium, but the oxidation is less easy than with the other platinum metals. (Berzelius.)

*Preparation.* 1. By heating nitrate of palladious oxide to low redness till the nitric acid is expelled.—2. By heating a palladious salt to commencing redness with carbonate of potash, and exhausting with water.

*Properties.* Black lumps, having the metallic lustre and the appearance of native black oxide of manganese, and yielding a black powder. (Berzelius.)

*Calculation*, according to Berzelius.

| | | | |
|---|---|---|---|
| Pd | 53·3 | .... | 86·95 |
| O | 8·0 | .... | 13·05 |
| PdO | 61·3 | .... | 100·00 |

(PdO = 665·899 + 100 = 765·899. Berzelius.)

*Decomposition.* Reduced to the metallic state at a red heat, with evolution of oxygen.

*Combinations. a.* With Water.—Hydrate of Palladious Oxide.—Formed by precipitating the aqueous solution of a palladious salt with carbonate of potash or soda. Caustic potash throws down a basic salt, which dissolves in excess of the alkali and forms a colourless solution. Dark brown precipitate, which gives off its water when gently ignited, but requires a higher temperature to reduce it to the metallic state. (Berzelius.)

*b.* With Acids, forming the Salts of Palladious Oxide, or Palladious Salts. — The anhydrous oxide dissolves in acids with difficulty, and only after long boiling; the hydrate is easily dissolved. The salts are for the most part brown and red. Their taste is astringent, but not metallic. (Fischer.) When ignited alone, or when gently heated in hydrogen gas, they yield metallic palladium. The metal is precipitated from the solutions of these salts by the following substances: By *phosphorus.* (Fischer, *Pogg.* 12, 504.)—By *sulphurous acid,* with the aid of heat. (Berzelius.)—By *nitrite of potash.* A solution of palladium likewise becomes covered with a metallic film, when immersed for a fortnight in nitrogen gas separated from the air by phosphorus, and afterwards washed. (Fischer, *Pogg.* 17, 137, and 480.)—By all the metals which reduce silver. In these reactions, it is immaterial whether the palladious oxide be dissolved in hydrochloric or in nitric acid; moreover, with the following exceptions, the nature of the metals makes but little difference. If part of the palladium be reduced by tin, the liquid acquires a brown tint, from admixture of stannous salt, and yields a brown precipitate; mercury likewise forms a brown precipitate, because mercurous nitrate yields a precipitate of that colour with palladious salts. Silver does not reduce palladium. (Fischer, *Pogg.* 10, 607.) By *green vitriol.* (Wollaston.) The precipitation does not take place for some time, and is still slower when the liquid contains excess of acid; the palladium is not deposited in the form of powder, but covers the sides of the vessel with a specular film. The reaction reaches its limit with 1 pt. of palladium in 1000 parts of liquid. (Fischer, *Schw.* 51, 197.) By boiling with *alcohol.* (Berzelius.) By *formiate of potash,* with the aid of heat, the metal is precipitated in shining laminæ. (Weiss & Döbereiner.)

Phosphuretted hydrogen gas throws down phosphide of palladium. This reaction distinguishes palladium from platinum, rhodium, and iridium, which are not precipitated by phosphuretted hydrogen. (Böttger, *Beiträge,* 2, 117.)—Hydrosulphuric acid and hydrosulphate of ammonia throw down dark brown sulphide of palladium, insoluble in excess of hydrosulphate of ammonia, but soluble in hydrochloric acid. 1 part of palladium in 10,000 parts of liquid still gives a brownish yellow colouring with hydrosulphuric acid. — Hydriodic acid and iodide of potassium throw down black iodide of palladium. In very dilute solutions, hydriodic acid first produces a dark brown-red colouring, and after a few hours, a black precipitate, the colour of the liquid becoming pale-red. (Pleischl, *Schw.* 43, 386.) 1 part of iodide of potassium dissolved in 5000 parts of water immediately forms a black precipitate with hydrochlorate of palladious oxide; in 50,000 parts of water it throws down a few black flakes after a while; and in 500,000 parts of water, nothing. (Baumann, *N. Br. Arch.* 29, 214.) 1 pt. of iodide of potassium in 400,000 parts of water still produces a brown colouring with iodide of potassium, and, after 20 hours,

throws down black flakes. (Lassaigne.) Since palladium-salts are not precipitated by bromide of potassium, the bromine may be obtained from the liquid filtered from the iodide of palladium and freed from palladium, by sulphuretted hydrogen. (O. Henry, *J. Pharm.* 28, 216; *comp.* L. A. Buchner, *Repert.* 78, 8.)

Protochloride of tin forms a black brown precipitate with palladious salts. (Wollaston.) Metallic tin acts in the same manner, after having first thrown down metallic palladium. In many cases, the liquid first acquires a red-brown tint. The black-brown precipitate dissolves in cold hydrochloric acid, forming a bluish green solution (hence an acid solution of palladium in hydrochloric acid, when mixed with protochloride of tin, becomes green at first, and afterwards deposits a brown powder); warm hydrochloric digested with the precipitate, dissolves out only the tin, and leaves the palladium in the form of a black powder. The tin-salt sometimes throws down a black powder and metallic films. Limit of the reaction: 1 pt. of palladium in 100,000 parts of liquid. (Fischer, *Schw.* 51, 197; 53, 113.) Mercurous nitrate forms at first a brown precipitate, which, together with the liquid, becomes darker after a while, and forms a metallic film on the sides of the vessel and on the surface of the liquid. The limit of the reaction is the production of a yellow colouring in a solution containing 1 pt. of palladium in 100,000 parts of liquid. (Fischer.)

Ammonia added in excess to palladious salts, forms a mixture which is yellow at first and colourless afterwards. (Berzelius.) It does not exhibit a blue colour unless copper is present. (Fischer, Berzelius.) A small quantity of ammonia forms no precipitate in a solution of the nitrate; but from the chloride, it throws down a copious flesh-coloured precipitate of ammonio-protochloride of palladium, soluble in a larger quantity of ammonia. Those palladious salts which are insoluble in water, are likewise soluble in ammonia. (Fischer.) Carbonate of ammonia behaves like pure ammonia. (H. Rose, *Analyt. Chem.*) If the hydrochloric solution does not contain any free acid, a large quantity of ammonia is required to dissolve the precipitate. (Fischer.) Potash or soda throws down a yellowish brown, gelatinous, basic salt, which redissolves in an excess of the alkali, forming a brown solution, according to Fischer, but colourless, according to Berzelius. Carbonate of potash or soda, and likewise baryta, strontia, and lime-water, behave in a similar manner. (Fischer.) The solution in excess of carbonate of potash becomes dark when boiled, and afterwards yields a brown precipitate: excess of carbonate of soda dissolves but little of it. (H. Rose.) ¶ In a more recent memoir (*Pogg.* 71, 431), Fischer states that potash or soda added to a solution of palladious nitrate, either neutral or acid, throws down a brown basic salt, insoluble in excess of the alkali. By boiling with excess of alkali, the whole of the acid is removed, and hydrated palladious oxide separated. In a cold solution of palladious nitrate containing excess of acid, potash produces no precipitate at first, but after a while, the same precipitate appears. Alkaline carbonates form no precipitate in either of these solutions at ordinary temperatures; but on boiling the liquid, nearly all the palladium is thrown down in the form of brown basic carbonate of palladious oxide. A solution of palladious sulphate behaves in the same manner, both with caustic alkalis and their carbonates. The chloride likewise exhibits the same character with alkaline carbonates; but caustic alkalis produce a precipitate, which, on the application of heat, dissolves in excess of the alkali, forming a light brown solution. Ammonia,

whether caustic or carbonated, behaves in a totally different manner. In a solutionof the nitrate, it produces a brown precipitate insoluble in excess, a considerable portion of the palladium, however, remaining dissolved, and forming a colourless solution. The sulphate, if neutral, is precipitated by ammonia, and the precipitate is easily soluble in excess. In a solution of the protochloride, excess of ammonia first produces a brown precipitate, which, on the addition of more ammonia, diminishes in quantity, and becomes peach-blossom coloured; a still larger quantity dissolves the precipitate, the solution taking place with facility on the application of heat. ¶

Phosphate and arseniate of soda form light-yellow precipitates with palladious salts. (Berzelius.) ¶ According to Fischer, phosphate of soda added to a solution of protochloride of palladium, produces, after a while, a brown precipitate of basic chloride; arseniate of soda gives no precipitate. ¶

Alkaline oxalates quickly throw down the palladium in the form of a yellow, fibrous oxalate; oxalic acid produces a similar effect in perfectly neutral solutions, but at the same time exerts a reducing action; so that after a while a metallic film is formed. (Fischer.) Alkaline tartrates and citrates form light yellow precipitates in the neutral solution of the nitrate. (Berzelius.) Cyanide of potassium or cyanide of mercury forms a yellowish white, gelatinous precipitate of cyanide of palladium, which becomes white after standing for some time, and is soluble in hydrochloric acid. (Wollaston.) Ferrocyanide and ferricyanide of potassium produce no precipitate at first, but after some time form a thick jelly. (H. Rose.) The former salt produces a yellowish brown precipitate (Fischer), the latter a red-brown. (Smee.) Gallic acid produces no effect. (Fischer.)

### B. Bioxide of Palladium, or Palladic Oxide. $PdO^2$.

Prepared by gradually pouring an aqueous solution of caustic or carbonated potash or soda on dry chloropalladiate of potassium, heating the mixture to the boiling point, and thoroughly washing the precipitated oxide.

Black.—Gives off its oxygen quietly at a red heat. (Berzelius.)

*Calculation*, according to Berzelius.

| | | | |
|---|---|---|---|
| Pd | 53·3 | .... | 76·92 |
| 2O | 16·0 | .... | 23·08 |
| $PdO^2$ | 69·3 | .... | 100·00 |

($PdO^2 = 665·899 + 200 = 865·899$. Berzelius.)

When heated, it gives off oxygen, and is reduced to the protoxide. (Berzelius.)

*Combinations.* *a.* With Water.—Hydrate of Palladic Oxide.—Chloropalladiate of potassium dissolves almost completely in cold aqueous caustic potash or soda, or their carbonates, forming a dark yellowish brown solution. This solution, when left to itself, becomes gelatinous, from separation of the greater part of the hydrated oxide; part of the oxide, however, remains dissolved, and imparts a yellow colour to the liquid. The dark yellowish brown hydrate, when washed with boiling water, turns black, and gives off part of its combined water; but the adhering potash is not quite removed by the washing. The hydrate, when heated, gives off water together with its second atom of oxygen, and with such violence, that it is thrown out of the retort. (Berzelius.)

*b.* With Acids, forming the Salts of Palladic Oxide, or Palladic Salts.—The hydrate, even when moist, dissolves but slowly in acids, forming a yellow solution; it dissolves without decomposition in concentrated hydrochloric acid, leaving, however, a residue of chloropalladiate of potassium, formed from the adhering potash; on the other hand, it gives off chlorine when treated with dilute hydrochloric acid. Hydrosulphuric acid reduces aqueous bichloride of palladium to protochloride, with precipitation of sulphur.

Nitrate of palladious oxide placed in the voltaic circuit, yields, at the positive pole, a peroxide of the metal, resembling peroxide of silver. (Fischer, *Kastn. Arch.* 16, 218.)

## Palladium and Carbon.

Carbide of Palladium.—*a.* Palladium fused in a crucible filled with lamp-black, becomes so brittle, that if struck with a hammer while red hot, it falls to powder, and gives off a white fume. (Bréant.)

*b.* Palladium-foil, held over the flame of a spirit-lamp—which deposits no soot on any other metal—becomes covered, in the inner part of the flame, where the heat does not rise above redness, with a black powder, which, when removed from the foil and burnt, leaves the palladium in the form of a grey powder. A piece of red-hot spongy palladium laid on the wick of a spirit-lamp just blown out, continues to glow (and produce acetic acid) as long as any alcohol remains, expanding at the same time to many times its original bulk, and throwing out cauliflower-like excrescences. This mass, when removed from the wick, burns in the air, and leaves a skeleton of palladium of the same form as the spongy palladium employed, but of ten times the bulk. A similar carboniferous palladium is formed by placing on the recently extinguished wick of the spirit-lamp a piece of palladium-foil previously ignited; whereupon the palladium continues to glow, as does also the carbonaceous mass formed upon it; and after the latter has burned away, there remains a skeleton of palladium, and under it the corroded foil. (Wöhler, *Pogg.* 3, 71); *comp.* H. B. Miller (*Ann. Phil.* 28, 20), who attributed this appearance to the formation of a peculiar oxide of palladium.

## Palladium and Phosphorus.

A. Palladium may be made to combine with phosphorus.

B. Neutral nitrate of palladious oxide forms a light yellow precipitate with alkaline phosphates. (Berzelius.) Aqueous phosphoric acid, boiled for a long time with palladium, deposits a shining metallic film as it cools; it must therefore have dissolved a portion of the metal, which, as the liquid cools, is again reduced by the resulting phosphorous acid. (Fischer.)

## Palladium and Sulphur.

A. Sulphide of Palladium.—1. The metal, when heated with sulphur, combines with it, and exhibits incandescence. (Berzelius.)—2. The sulphide is also formed by heating ammonio-protochloride of palladium with sulphur. (Vauquelin.)—3. By precipitating a palladious salt with sulphuretted hydrogen, washing the precipitate quickly on the filter with boiling water, and drying it in vacuo over oil of vitriol.

(Fellenberg, *Pogg.* 50, 65.) By (1) and (2): bluish white, with metallic lustre, very hard; fracture shining and laminated; fuses at the melting point of silver. (Vauquelin). By (3): black-brown.

| | | | | Fellenberg. | Berzelius. | Vauquelin. |
|---|---|---|---|---|---|---|
| Pd | 53·3 | 76·91 | | 75·65 | 78 | 80·6 |
| S | 16·0 | 23·09 | | 24·35 | 22 | 19·4 |
| PdS | 69·3 | 100·00 | | 100·00 | 100 | 100·0 |

When heated to redness in the air, it is very slowly converted into basic sulphate of palladious oxide (Berzelius), and at a higher temperature is reduced to pure palladium. (Berzelius, Vauquelin.) When heated in a current of chlorine-gas, it yields chloride of sulphur, which distils over, and protochloride of palladium, part of which sublimes, and forms a rose-coloured sublimate, while the rest remains behind in the form of garnet-coloured, crystalline globules. 100 parts of sulphide of palladium yield 127·6 parts of chloride. (Fellenberg.)

B. Sulphate of Palladious Oxide, or Palladious Sulphate.—*a. Basic.*—Formed by gently igniting the sulphide in contact with air. Brown-red, reducible at a strong heat, easily soluble in hydrochloric acid. (Berzelius.)

*b. Monosulphate.*—1. By boiling palladious nitrate with sulphuric acid. Red, soluble in water. (Berzelius.) Oil of vitriol does not act on palladium in the cold, but when heated, dissolves it, with evolution of sulphurous acid, and forms a yellowish red solution, which, if saturated, deposits the neutral salt, as it cools, in the form of a red powder; this powder dissolves with tolerable facility in water, forming a yellow solution. (Fischer.) ¶ The coherent hammered metal is not attacked by sulphuric acid; but spongy or pulverulent palladium dissolves in it when heated, forming a brown solution; and if the heat be continued, the salt separates in the form of a brown powder. But the neutral sulphate cannot be obtained in this manner, because the heat required to drive off the excess of acid produces decomposition. (Fischer, *Pogg.* 81, 431.) ¶

## Palladium and Selenium.

Selenide of Palladium.—Combination between these substances takes place easily, and is attended with evolution of heat. The compound is grey and infusible, gives off selenium before the blowpipe, and yields a seleniferous, greyish white, brittle, crystalline metallic button. (Berzelius.)

## Palladium and Iodine.

A. Iodide of Palladium.—Palladium-foil turns black when an alcoholic solution of iodine is evaporated to dryness upon it: this reaction distinguishes palladium from platinum, which remains bright when thus treated. (Berzelius.) Similarly, palladium-foil heated in iodine vapour becomes covered with coloured films, and afterwards turns brown; the application of heat or treatment with ammonia restores its brightness. Iodine heated in a glass tube with finely divided palladium, combines but imperfectly with it; and again, when palladium-foil is boiled with iodine

and water, or with hydriodic acid and nitric acid, part of it remains unaltered. (Lassaigne.)

Iodide of palladium is obtained in the form of a black, tasteless, and inodorous mass, by precipitating a palladious salt with iodide of potassium, washing with boiling water, and drying the black gelatinous flakes for 24 hours in vacuo. (Lassaigne, *J. Chim. méd.* 11, 57.)

| | | | | Lassaigne. |
|---|---|---|---|---|
| Pd | 53·3 | 29·73 | | 29·72 |
| I | 126·0 | 70·27 | | 70·28 |
| PdI | 179·3 | 100·00 | | 100·00 |

Iodide of palladium gives off its iodine between 300° and 360°. Boiling potash decomposes it, with separation of a black powder consisting of palladious oxide. It is insoluble in water, alcohol, ether, and aqueous hydriodic acid (thereby distinguished from platinum). (Lassaigne.)

*Hydrated Iodide of Palladium.*—The precipitate formed by iodide of potassium in palladious salts, if merely dried in the air, instead of being desiccated for a long time in vacuo, shrinks up to a black friable mass having a smooth, conchoidal fracture, and retains 5·05 p. c. (1 At.) o water. (Lassaigne.)

B. Iodate of Palladious Oxide.—Iodic acid forms with aqueous protochloride of palladium, a scanty yellowish precipitate; iodate of potash, a more copious one. (Pleischl.)

## Palladium and Bromine.

A. Bromide of Palladium.—Palladium dissolved in a mixture of hydrobromic and nitric acid yields, on evaporation, a chestnut-brown mass, insoluble in water, but soluble in aqueous hydrobromic acid. Bromide of palladium forms dark brown salts with basic metallic bromides. (Bonsdorff, *Pogg.* 19, 347.)

B. Bromate of Palladious Oxide.—Hydrated palladious oxide dissolves but very sparingly in aqueous bromic acid.

## Palladium and Chlorine.

A. Protochloride of Palladium, or Palladious Chloride.—1. Formed by evaporating to dryness the solution of palladium in aqua-regia, and de-hydrating the residue by a gentle heat. (Berzelius.)—2. By heating sulphide of palladium in a stream of chlorine gas. (Fellenberg, p. 347.) When prepared by (1), it is black-brown, and fuses without decomposition when gently heated in a glass vessel. When fused in a platinum vessel, it acquires a bluish green colour, by taking up protochloride of platinum. (Berzelius.) The second process yields a rose-coloured sublimate, together with a non-sublimed, garnet-coloured, crystalline mass. (Fellenberg.) ¶ By evaporating the hydrochloric acid solution over quick lime, the chloride is obtained in red-brown, prismatic crystals, which, if free from nitric acid, remain perfectly dry. (Fischer.)

| | | | | Fellenberg. |
|---|---|---|---|---|
| Pd | 53·3 | 60·09 | | 60·2 |
| Cl | 35·4 | 39·91 | | 39·8 |
| PdCl | 88·7 | 100·00 | | 100·0 |

When strongly heated, it is resolved into chlorine gas and metallic palladium. (Berzelius.) Heated in a current of hydrogen, it is easily decomposed, yielding palladium and hydrochloric acid. (Fellenberg.) With basic metallic chlorides, it forms brown chlorine-salts, easily soluble both in water and in alcohol.

*Aqueous Protochloride of Palladium*, or *Hydrochlorate of Palladious Oxide.*—1. Protochloride of palladium prepared by (2) dissolves slowly but completely in water, forming a deep yellowish-red liquid. (Fellenberg.)—2. Palladium dissolves gradually in hydrochloric acid, if the air has access to it. (Fischer.)—¶ Even the hammered metal dissolves quickly in hydrochloric acid, if chlorine gas be likewise passed into the liquid; if nitric acid be added, nitrate is formed as well as chloride. (Fischer.) ¶—3. When palladium is dissolved in aqua-regia and the excess of acid expelled by evaporation, there remains a brownish yellow crystalline mass, slightly soluble in water. (Vauquelin.) The aqueous solution is yellow; if, however, it contains excess of hydrochloric acid, which greatly increases the solubility of the chloride, it is brown-red (Vauquelin); according to Fischer, the neutral solution is yellowish brown. The solution mixed with caustic potash, or carbonate of potash, yields red flakes, but remains coloured till the whole is precipitated by heat. (Vauquelin.) Lime-water in the dark precipitates it but partially, and the filtrate, when exposed to sunshine, still gives a precipitate, which appears to be composed in a similar manner to the platinum precipitate. (Fr. Döbereiner, *Ann. Pharm.* 14, 253.) Alcohol throws down from the solution a black, pulverulent, basic salt [the metal?], while the acid salt remains dissolved, and imparts a brown colour to the liquid. (Fischer.)

B. Palladious Oxychloride, or Basic Hydrochlorate of Palladious Oxide.—When the aqueous solution of protochloride of palladium is repeatedly evaporated to dryness, part of the hydrochloric acid escapes, and a basic salt is left in the form of a dark rose-coloured powder, insoluble in water. (Berzelius.) When a solution of palladium in aqua-regia is evaporated to dryness at a gentle heat, water dissolves but a small portion of the residue, and the yellow filtrate soon becomes turbid, and deposits the whole of the palladium in the form of a brown basic salt. (Fischer.)

C. Bichloride of Palladium, or Palladic Chloride.—Known only in combination with water or with basic metallic chlorides. When protochloride of palladium is dissolved in concentrated aqua-regia, and the liquid gently heated, a black-brown solution is obtained, which, when mixed with chloride of potassium, forms a red precipitate of chloropalladiate of potassium, while chloropalladite of potassium remains in solution. The solution of palladium in strong aqua-regia contains protoxide for the most part; but a small quantity of the bioxide is likewise present in it, so that on the addition of chloride of potassium, a precipitate of chloropalladiate of potassium is obtained. The bichloride may also be obtained in solution by dissolving the hydrated bioxide in concentrated hydrochloric acid. The potash in the hydrated oxide gives rise to the formation of chloropalladiate of potassium, which remains undissolved. Brown liquid, which gradually gives off chlorine, especially on dilution or evaporation, and is thereby converted into hydrochlorate of palladious oxide. (Berzelius.)

## Palladium and Nitrogen.

A. Nitrate of Palladious Oxide, or Palladious Nitrate.—Palladium dissolves less quickly in pure nitric acid than in that which is mixed with nitrous acid. (Wollaston.) Nitric acid acts slowly in the cold, and becomes charged with nitrous acid, without giving off nitric oxide; when heated, it acts more quickly, and gives off nitric oxide, but a large quantity of nitric acid is required to dissolve the metal. (Fischer.) The dark brown solution dries up to a brown-red mass. (Wollaston.) This, when ignited, leaves palladious oxide. (Berzelius.) The salt obtained by evaporating the solution to dryness forms with water a dark brown solution, which is sometimes turbid from the first, sometimes becomes so after a short time, and gradually deposits nearly all the palladium in the form of a brown basic salt. Alcohol added to this solution likewise throws down a black powder. (Fischer.)

B. Ammonio-protiodide of Palladium.—*a. With* 2 *At. Ammonia.*—1. The solution of *b* ($NH^3$,PdI) in hot concentrated ammonia, if evaporated in an atmosphere of ammoniacal gas, or with constant addition of ammonia, yields white crystals.—2. The same substance is formed by saturating with ammonia either the compound *b*, or iodide of palladium; 179·3 parts (1 At.) of the latter take up 34·8 (2 At.) of ammonia, turning white at the same time. The crystals, when exposed to the air, quickly give off water and turn yellowish; even in close vessels, they become yellowish-red in the course of six months. (Fehling.)

| | *Crystallized.* | | | Fehling. |
|---|---|---|---|---|
| 2N | 28·0 | 13·13 | | 12·56 |
| 6H | 6·0 | 2·81 | | 2·73 |
| Pd | 53·3 | 24·99 | | 24·77 |
| I | 126·0 | 59·07 | | 58·64 |
| $2NH^3$,PdI | 213·3 | 100·00 | | 98·70 |

*b. With* 1 *At. Ammonia.*—The colourless solution of iodide of palladium in ammonia deposits orange-yellow crystals when exposed to the air. Acids, which saturate the excess of ammonia, throw down an orange-yellow powder having the same composition. (Lassaigne, *J. Chim. méd.* 11, 62.) Protiodide of palladium dissolves easily and with rise of temperature, even in dilute ammonia, leaving only a few flakes. The pale yellow solution, mixed with hydrochloric or any other acid, suddenly becomes dark-coloured, and deposits a reddish yellow powder, which, after being quickly washed, must be pressed between blotting paper frequently renewed, and then dried in vacuo over warm sand. The compound resembles chloroplatinate of ammonium contaminated with chloriridiate of ammonium. It is permanent in the dry state, but, when moist, is rapidly transformed into a red crystalline mass, having the same composition. This conversion often begins even during washing, or while the compound is undergoing desiccation either in vacuo or by heat—unless it has been previously pressed between paper—and is completed in a few days. The reddish yellow compound is likewise converted into the red crystalline modification by continued boiling with water, or by a trace of ammonia going off at the same time, and the water, when evaporated, deposits a reddish substance. Boiling nitric acid dissolves the reddish yellow compound with evolution of iodine, and converts it into palladious nitrate. (Fehling, *Ann. Pharm.* 39, 116.)

| | | | | | Fehling. |
|---|---|---|---|---|---|
| N | 14·0 | .... | 7·13 | ..... | 7·19 |
| 3H | 3·0 | .... | 1·53 | ..... | 1·57 |
| Pd | 53·3 | .... | 27·15 | ..... | 27·35 |
| I | 126·0 | .... | 64·19 | ..... | 64·18 |
| $NH^3$,PdI | 196·3 | .... | 100·00 | ..... | 100·29 |

C. Ammonio-protochloride of Palladium.—*a. With* 2 *At. Ammonia—a. Anhydrous.*—100 parts of the yellow compound C, *b*, *β*, absorb from 15·57 to 16·73 parts of dry gaseous ammonia. (Fehling.)

*β. Hydrated.*—1. 100 parts of the yellow compound C, *b*, *β*, quickly absorb from 24·15 to 24·71 parts (1 At.) of moist ammoniacal-gas, the colour changing to white, and the absorption being complete in 24 hours. The red compound C, *b*, *a*, absorbs moist ammonia very slowly, but does not take up quite 1 At. of it, even in several weeks; its colour also changes only to dirty white.—2. The solution of either the yellow or the red compound in aqueous ammonia, if evaporated with frequent addition of ammonia, yields white crystals, likewise consisting of $2NH^3$,PdCl,HO. The white compound heated to 120° gives off 1 At. ammonia and 1 At. water. The crystals are easily soluble in water, and acids added to the solution throw down, after a few minutes, remarkably fine crystals of the yellow compound C, *b*, *β*. (Fehling.)

| | *a. Anhydrous.* | | | *β. Hydrated.* | | | Fehling. |
|---|---|---|---|---|---|---|---|
| $2NH^3$ | 34·0 | .... | 27·71 | $2NH^3$ .... | 34·0 | .... 25·82 | .... 25·77 |
| PdCl | 88·7 | .... | 72·29 | PdCl .... | 88·7 | .... 67·35 | .... |
| | | | | HO | 9·0 | .... 6·83 | .... |
| $2NH^3$,PdCl | 122·7 | .... | 100·00 | + Aq. .... | 131·7 | .... 100·00 | |

*b. With* 1 *At. Ammonia.—a. Red.*—Discovered by Vauquelin.—1. Obtained in the course of Vauquelin's treatment of platinum ore (p. 257, No. 14).—2. A moderately concentrated solution of protochloride of palladium forms the same red precipitate with a slight excess of ammonia. (Vauquelin, Fehling.)—Soft, rose-coloured scales. (Vauquelin.) When heated to 100° in the moist state, it is for the most part converted into the following yellow compound *β*; in the dry state, on the contrary, it retains its colour at 180°, but at 200°, turns yellow, without loss of weight, assuming, however, a paler colour than it does when water is present. (Fehling.) At a higher temperature, it fuses, giving off sal-ammoniac and chlorine [or perhaps hydrochloric acid and nitrogen gas], and leaves from 40 to 42 per cent. of metal. (Vauquelin.) Insoluble in cold water. (Fischer, Fehling.) Dissolves in boiling water, undergoing decomposition, and leaving a small brown residue. This residue contains 64·18 per cent. of palladium and 14·85 per cent. of chlorine; if the deficient 20·97 per cent. be reckoned as ammonia, the residue must be supposed to consist of $Pd^3Cl$,$3NH^3$; but the analysis was made with too small a quantity to render it worthy of much reliance. The aqueous decoction, on cooling, deposits the following yellow compound—which may likewise be precipitated by hydrochloric or nitric acid—and retains sal-ammoniac in solution. (Fehling.) It dissolves in water containing hydrochloric acid, slowly in the cold, quickly when heated, and forms a solution of chloropalladiate of ammonium. (Vauquelin.) It dissolves easily in rather concentrated hydrochloric or nitric acid, forming a brown solution. (Fischer.) From the nitric acid solution, ammonia re-precipitates the red crystals; and the nitric acid solution, when evaporated to dryness, leaves a brown red residue, easily soluble in water, and probably consisting

of a mixture of palladious nitrate and ammoniacal salt. (Fehling.) It dissolves in ammonia only after continued boiling; acids added to the solution throw down the yellow compound. (Fischer, Fehling, *Ann. Pharm.* 39, 110.)

*β. Yellow.*—First obtained by Fischer.—1. Formed by supersaturating aqueous protochloride of palladium with a quantity of ammonia sufficient to redissolve the precipitate, and evaporating—or, better, by treating the solution with a sufficient quantity of hydrochloric acid to precipitate the compound. The same treatment may likewise be adopted with the solution of the red compound or of chloropalladite of ammonium. (Fischer.) Berzelius likewise supersaturates the aqueous solution of protochloride of palladium with ammonia, and evaporates the solution, which is yellow at first, but afterwards becomes colourless, to dryness; on digesting the residue in water, the yellow compound remains undissolved. When the red compound is prepared by (2), and the liquid filtered from it is mixed with hydrochloric or nitric acid, a precipitate of the yellow compound is likewise formed. (Fehling.)—2. The red compound is converted into the yellow by heat (Fehling, p. 351); also by olution in ammonia and re-precipitation by hydrochloric acid. (Fischer.)

Yellow powder, consisting of fine needles (Fischer); yellow crystalline (Fehling); light lemon-yellow crystalline powder (Lampadius); yellowish green (Berzelius).

When heated in a retort, it first gives off ammonia, then hydrochloric acid and nitrogen gas, and, finally, sal-ammoniac; while 50 per cent. of palladium remains behind. (Berzelius.) The salt, when thus treated, first turns green, and then yields grey metallic palladium. (Lampadius.) Insoluble in water; sparingly soluble in hydrochloric or nitric acid, and only when heated; dissolves easily in cold ammonia. (Fischer, *Schw.* 51, 201.) On boiling the compound with water; and then leaving it to cool for several hours till its temperature falls to 16°, one part of it remains dissolved in 382 parts of water. (Lampadius.) Dissolves in nitric acid, and forms a brown solution, which behaves like the nitric acid solution of the red compound. Dissolves in ammonia much more easily than the red compound, and is again precipitated yellow by acids. (Fehling.)

| | *Red* or *yellow Compound.* | | Fehling. | | Berzelius. | Lampadius. |
|---|---|---|---|---|---|---|
| | | | *Red.* | *Yellow.* | *Yellow.* | *Yellow.* |
| N | 14·0 | 13·24 | 12·26 | 13·12 | | |
| 3H | 3·0 | 2·84 | 2·83 | 3·22 | | |
| Pd | 53·3 | 50·43 | 50·51 | 50·35 | 50·00 | 50·27 |
| Cl | 35·4 | 33·49 | 32·55 | 32·83 | | |
| $NH^3$,PdCl | 105·7 | 100·00 | 98·15 | 99·52 | | |

D. Chloropalladite of Ammonium.—First obtained by Wollaston. —1. A solution of palladious oxide in hydrochloric acid is mixed with sal-ammoniac, and evaporated to the crystallizing point. (Wollaston.) The solution must contain an excess of acid; otherwise, nothing but a mixture of sal-ammoniac and chloride of palladium will be obtained. (Fischer.)—2. The red variety of ammonio-protochloride of palladium is dissolved in hydrochloric acid, and the liquid evaporated. (Fischer.) The wash-water of the ammonio-protochloride of palladium obtained by the process described in No. 14, p. 257, often yields these crystals on evaporation. (Vauquelin.) Yellowish green, four-sided, and, according to Vauquelin, six-sided prisms and needles, exhibiting a peculiar play of colours. (Wollaston.) Dissolves easily in water, forming a dark red, or, according

to Fischer, a yellowish brown solution. Insoluble in strong alcohol (Wollaston, *A. Gehl.* 5, 186), but slightly soluble in that which contains water. (Fischer.)

E. Chloropalladiate of Ammonium. — Formed by mixing the solution of palladium in aqua-regia with sal-ammoniac, and evaporating at a gentle heat. The substance which remains is similar to the corresponding potassium compound, and like that substance, sparingly soluble in water. (Berzelius.)

F. Nitrate of Palladious Oxide and Ammonia.—When palladious nitrate is evaporated to dryness, and the residue boiled with excess of ammonia, the basic compound *a* separates out, while the neutral compound *b* remains in solution.

*a.* Dark brown powder, exhibiting the metallic lustre. Dissolves easily in hydrochloric acid, and leaves crystals of ammonio-protochloride of palladium on evaporation. Dissolves in hot, but not in cold nitric acid. Insoluble in water, and also in ammonia, even at a boiling heat. (Fischer.)

*b.* May also be obtained by adding ammonia to an acid solution of palladious nitrate, till the precipitate is redissolved, and evaporating the greenish brown solution (colourless, according to Berzelius) to the crystallizing point. Crystals of nitrate of ammonia mix with the product, their quantity being larger in proportion to the excess of acid in the original solution; but they are easily separated, in consequence of their deliquescence and easy solubility in water. Transparent and colourless, shining, four-sided prisms and laminæ. (Fischer.) When the solution is evaporated to dryness, the compound remains in pearly scales. (Berzelius.) When heated, it fuses and detonates slightly, with emission of light. Decomposed by hydrochloric acid, which soon separates from it the yellow ammonio-protochloride of palladium (p. 351). Easily soluble in water. With nitric acid it forms a clear yellow solution. Dissolves easily in ammonia, forming a colourless solution. Insoluble in alcohol. (Fischer.)

## Palladium and Potassium.

A. Sulphate of Palladious Oxide and Potash.—Palladium, like rhodium, dissolves in fused bisulphate of potash. (Berzelius.)

B. Iodopalladite of Potassium.—The wine-red solution of protiodide of palladium in aqueous iodide of potassium, yields, on evaporation, blackish grey, deliquescent cubes. (Lassaigne, *J. Chim. méd.* 11, 61.)

C. Bromopalladite of Potassium.—The mixed solution of protobromide of palladium and bromide of potassium, yields, on evaporation, dark brown needles, which are permanent in the air, and form a dark brown solution in water. (Bonsdorff, *Pogg.* 19, 347.)

D. Chloropalladite of Potassium. — 1. Formed by dissolving palladium in hydrochloric acid mixed with nitre. (Wollaston.)—2. By mixing a solution of palladium in aqua-regia, freed by evaporation from excess of acid, with chloride of potassium. If the solutions are strong, the salt is immediately precipitated in golden-yellow needles; if they are more dilute, it crystallizes on evaporation. (Berzelius.) Four-sided prisms, which appear red when viewed by light transmitted along the axis, but

light-green in all other directions. (Wollaston.) Their crystalline form is the same as that of the corresponding platinum-salt (p. 322). The prisms are greenish brown, and exhibit no appearance of dichroism. When heated, they fuse, with some loss of chlorine; and on cooling, solidify in crystals, having the same form and colour, but leaving a certain quantity of palladium when dissolved in water. They cannot be completely separated from mechanically adhering water by heat, because a portion of the hydrochloric acid goes off with the water, and palladious oxide is consequently set free. (Berzelius.) When the compound is heated to redness, the palladium remains, in scales united in spongy masses, together with chloride of potassium. (Biewend.) Sulphurous acid or alcohol reduces the palladium at a boiling heat. (Berzelius.) The colourless solution of the salt in ammonia yields, on evaporation, colourless needles, mixed with a yellow powder, into which also the entire mass is converted when evaporated by heat. This yellow powder, in addition to ammonia and chlorine, contains 57·5 per cent. of palladium. (Berzelius.) The salt dissolves easily, and with a dark red colour, in water, but not in alcohol. (Wollaston.) It dissolves even in spirit of sp. gr. 0·84, but very sparingly in absolute alcohol, by which indeed it is precipitated from a solution saturated while hot, in golden-yellow shining laminæ. From the solution in hydrated alcohol the metal is precipitated on boiling. (Berzelius.)

| | *Crystallized.* | | Berzelius. |
|---|---|---|---|
| KCl | 74·6 | 45·68 | 45·89 |
| Pd | 53·3 | 32·64 | 32·69 |
| Cl | 35·4 | 21·68 | 21·42 |
| KCl,PdCl | 163·3 | 100·00 | 100·00 |

According to Thomson, it contains 26·4 potash, 35·2 palladious oxide, 35·61 hydrochloric acid, and 2·79 water.

E. Chloropalladiate of Potassium.—When a solution of chloropalladite of potassium in aqua-regia is evaporated, nitric oxide is given off, and this compound separates in small regular octohedrons, which are vermilion-coloured when very small, but brown-red when somewhat larger. Chloropalladiate of potassium, when heated, fuses, gives off chlorine, and is converted into chloropalladite of potassium. Aqueous ammonia decomposes it, with evolution of nitrogen, and likewise converts it into chloropalladite of potassium. When boiled with alcohol, which has no action upon it in the cold, it is decomposed, with evolution of ethereal vapours. When boiled with water, it gives off chlorine, and deposits hydrated palladic oxide, the liquid retaining free hydrochloric acid; by longer boiling, it is completely reduced to chloropalladite of potassium. In a stoppered bottle, however, it dissolves in boiling water, forming a dark-coloured solution, from which it separates out on cooling, the separation being attended with partial decolorization of the liquid, which still retains chloropalladite of potassium and free chlorine. In cold water, it dissolves with difficulty, forming a yellow solution, which contains a small portion of undecomposed salt, but mainly consists of chloropalladite of potassium and free chlorine. The chloropalladiate dissolves without decomposition in dilute hydrochloric acid, and is left unaltered when the liquid is evaporated. It is insoluble in water containing sal-ammoniac, chloride of potassium, or common salt, and likewise in alcohol. (Berzelius.)

F. Fluopalladite of Potassium.—Precipitated on mixing palladious

nitrate with fluoride of potassium. Light yellow, sparingly soluble in water. (Berzelius.)

¶ G. Nitrite of Palladious Oxide and Potash.—Formed by adding nitrite of potash to a solution of protochloride of palladium, till the brown colour changes to yellow, and evaporating the liquid to dryness. Forms yellow prismatic crystals. (Fischer.) ¶

### Palladium and Sodium.

A. Chloropalladite of Sodium.—Red, deliquescent, soluble in alcohol. (Wollaston.)

B. Fluopalladite of Sodium.—Similar to the potassium-salt.

¶ C. Nitrite of Palladious Oxide and Soda.—Fibrous salt, obtained in a similar manner to the corresponding potassium-compound. (Fischer.) ¶

### Palladium and Barium.

A. Alloy of Palladium and Barium.—The two metals unite before the oxy-hydrogen blowpipe. Silver-white; becomes covered with oxide in the course of 24 hours. (Clarke, *Gilb.* 62, 373.)

B. Bromopalladite of Barium.—Dark brown needles, permanent in the air, and forming a dark brown solution in water. (Bonsdorff.)

C. Chloropalladite of Barium.—A solution of palladium in aqua-regia is mixed with chloride of barium and evaporated to dryness, to drive off the excess of acid—the residue dissolved in water—and the solution left to evaporate under a bell-jar, in a vessel standing over oil of vitriol. Brown, effloresced radiating, crystals and dendrites, easily soluble both in water and in alcohol. (Bonsdorff.)

### Palladium and Calcium.

A. *Palladite of Lime?*—Hydrochlorate of palladious oxide saturated with lime-water, and filtered in the dark, yields, on exposure to sunshine, a precipitate containing lime. (Fr. Weiss & Fr. Döbereiner.)

B. Chloropalladite of Calcium.—Light brown, deliquescent prisms, soluble in alcohol. (Bonsdorff.)

### Palladium and Magnesium.

Chloropalladite of Magnesium.—Brown needles, which deliquesce in rather damp air, and are soluble in alcohol. (Bonsdorff.)

### Palladium and Manganese.

A. Bromopalladite of Manganese.—Dark brown needles, permanent in the air, and forming with water a solution of the same colour. (Bonsdorff.)

B. Chloropalladite of Manganese.—Brown-black cubes, permanent in the air, or rhombohedrons, nearly approaching to the cubical form; soluble in water and alcohol. (Bonsdorff.)

### Palladium and Arsenic.

A. Arsenide of Palladium.—Combination between these metals is attended with evolution of heat. (Fischer.) The alloy is brittle and fusible. (Chenevix.)

B. Arseniate of Palladious Oxide.—Neutral nitrate of palladious oxide forms a light yellow precipitate with alkaline arseniates. (Berzelius.)

### Palladium and Antimony.

Antimonide of Palladium.—These two metals form a brittle alloy, the combination being attended with evolution of light and heat. (Fischer.)

### Palladium and Bismuth.

Alloy.—Formed of equal portions of the two metals. Grey, brittle, nearly as hard as steel; sp. gr. 12·587. (Chenevix.)

### Palladium and Zinc.

A. Alloy.—These two metals form a brittle alloy, the combination being attended with evolution of light and heat. (Fischer.)

B. Bromopalladite of Zinc.—Dark brown compound, which forms with water a solution of the same colour. (Bonsdorff.)

C. Chloropalladite of Zinc.—Very deliquescent needles, of a chestnut-brown colour, and united in radiated masses. (Bonsdorff.)

### Palladium and Cadmium.

Chloropalladite of Cadmium.—Light brown, delicate needles, permanent in the air.

### Palladium and Tin.

Alloy.—Combination takes place with evolution of light and heat.

(Fischer.) In equal parts: Greyish white, softer than bar-iron, very brittle; fracture fine-grained; sp. gr. 8·175. (Chenevix.)

### Palladium and Lead.

Alloy.—Combination between these metals is attended with evolution of light and heat. (Fischer.) Grey, very hard and brittle; fracture fine-grained; sp. gr. 12·0. (Chenevix.)

### Palladium and Iron.

A. Alloy.—Brittle.

B. Carbide of Palladium and Iron.—1 part of palladium forms, with 100 parts of steel, an alloy which is well adapted for cutting instruments requiring a perfectly smooth edge. (Faraday & Stodart.)

### Palladium and Nickel.

A. Alloy.—The two metals unite before the oxy-hydrogen blowpipe. The alloy has a remarkably strong lustre, and is very extensible. (Clarke, *Gilb.* 62, 359.)

B. Chloropalladite of Nickel.—Greenish brown rhombohedrons, or perhaps very slightly inclined prisms; permanent in rather dry air. (Bonsdorff.)

### Palladium and Copper.

Alloy.—Combination takes place without evolution of light and heat. (Fischer.) 4 parts of copper with 1 part of palladium form a white, ductile alloy. (Cock.) Equal parts of the two metals form a yellowish grey, brittle alloy, harder than bar-iron, and of specific gravity 10·392. (Chenevix.) Equal volumes of the two metals heated together before the oxy-hydrogen blowpipe form a pale-coloured alloy, which takes a very high polish, is easily attacked by the file, and fuses with tolerable facility. (Clarke.)

### Palladium and Mercury.

Amalgam of Palladium.—By decomposing the aqueous solution of a palladium-salt with excess of mercury, agitating the two together for a considerable time, a soft amalgam is obtained. (Wollaston.) If the palladium-salt is in excess, the amalgam takes the form of a grey powder, which contains 2 At. palladium to 1 At. mercury, and does not give up its mercury at a red heat, but only when heated to whiteness. (Berzelius.)

### Palladium and Silver.

Alloy.—Combination between these two metals is not attended with evolution of light and heat. (Fischer.) The alloy formed of equal weights

of the two is grey, harder than silver, softer than iron, and has a specific gravity of 11·29. (Chenevix.)

### Palladium and Gold.

Alloy of Gold and Palladium.—The two metals combine without evolution of light and heat. (Fischer.)—*a.* 1 pt. of palladium to 1 pt. of gold: Grey, as hard as bar-iron, but less ductile than either of the component metals; fracture coarse-grained; sp. gr. 11·079. (Chenevix.)—*b.* 1 pt. palladium to 4 pts. gold: White, hard, ductile. (Cock.)—*c.* 1 pt. palladium to 6 pts. gold: Nearly white. (Wollaston.)

B. Alloy of Gold, Silver, and Palladium.—The *Oro pudre* (impure gold) from Porpez in South America consists of grains of gold, with numerous edges, and of an impure gold colour; they fuse before the blowpipe, without imparting any colour to borax, and are malleable after cooling. (Berzelius, *Pogg.* 35, 514.)

| | Berzelius. |
|---|---|
| Ag | 4·17 |
| Pd | 9·85 |
| Au | 85·98 |
| | 100·00 |

### Palladium and Platinum.

Alloy.—Equal weights of the two metals unite somewhat below the melting point of palladium, and form a grey alloy, having the hardness of bar-iron, and a specific gravity of 15·141; it is less ductile than the alloy of gold and palladium. (Chenevix.)

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## Chapter XLI.

# RHODIUM.

*Besides the Memoirs cited on p.* 252:

Wollaston. *Phil. Trans.* 1804, 419; also *Gilb.* 5, 175.
Vauquelin. *Ann. Chim.* 88, 167; also *Schw.* 12, 265.
Berzelius. *Ann. Phil.* 3, 252; also *Schw.* 22, 317. *Pogg.* 13. 437.

*History.* Discovered by Wollaston in 1804; examined principally by Berzelius.

*Sources.* In the platinum ore of South America, Domingo, and the Ural (p. 254); in the Peruvian ore, according to Wollaston, it amounts to only $\frac{1}{250}$.

*Preparation.* According to Wollaston (pp. 256, 257, No. 10); according to Vauquelin (p. 257, as far as No. 16); according to Berzelius (pp. 260, 261, Nos. 9 and 17, and p. 265, No. 17—20).

*Properties.* Specific gravity, somewhat above 11·00. (Wollaston.) According to Vauquelin, it is a grey powder, which does not fuse upon charcoal ignited in a stream of oxygen gas, but becomes somewhat coherent, silver-white, and brittle. According to Faraday & Stodart (*Ann. Chim. Phys.* 21, 63) it fuses imperfectly in the forge-fire. According to Cloud, it fuses before the oxy-hydrogen blowpipe into a steel-grey, hard, brittle globule, having a density of 11·2. According to Clarke (*Ann. Phil.* 17, 424), rhodic oxide and chloride of rhodium ignited in the oxy-hydrogen blowpipe flame, yield a silver-coloured, perfectly malleable globule, combustion taking place at the same time, accompanied by a green light, and part of the metal volatilizing. In former trials Clarke obtained only a partially malleable bead.

## *Compounds of Rhodium.*

### Rhodium and Oxygen.

### A. Protoxide of Rhodium, or Rhodious Oxide. RO.

Formed by igniting the metal in contact with air. Under these circumstances, 100 parts of rhodium quickly increase, by conversion into protoxide, to 115·3 parts; then slowly, if the ignition be continued, to 118·07 parts, a black powder being formed, consisting of $3RO,R^2O^3$. (Berzelius.)

Black powder, which does not acquire the metallic lustre by pressure.

| | | | |
|---|---|---|---|
| R ..... | 52 | .... | 86·67 |
| O ..... | 8 | .... | 13·33 |
| RO ..... | 60 | .... | 100·00 |

(RO = 651·387 + 100 = 751·387. Berzelius.)

Reduced by very strong ignition, but oxidates again at a lower temperature. When heated with sugar, it is reduced with slight detonation, but oxidates again, if quickly removed from the fire. (Berzelius.)

### B. Rhodioso-rhodic Oxide.

*a.* $3RO,R^2O^3$.—The powder obtained by continued ignition of pulverulent rhodium in contact with the air. (Berzelius.)

*b.* $2RO,R^2O^3$.—By decomposing $\frac{5}{4}$-chloride of rhodium with boiling potash, a gelatinous, yellowish brown-grey hydrate is obtained, which must be composed of $2RO,R^2O^3$, but contains likewise a small quantity of potash. It is but slightly altered by cold hydrochloric acid, which colours it yellow; but the same acid, at a boiling heat, turns it red, and converts it into sesquichloride of rhodium, which dissolves, and protochloride, which for the most part remains undissolved. The hydrate dissolves in excess of potash, forming a yellow solution.

*c.* $2RO,3R^2O^3$?—When a mixture of chlororhodiate of potassium and excess of carbonate of soda is heated not quite to redness, a gas is evolved containing 1 volume of oxygen and from 21 to 26 volumes of carbonic acid. (Berzelius.) Supposing now that the real proportion by volume of

the carbonic acid to the oxygen is 24 : 1, the proportion in atoms will be 12 : 1 (inasmuch as carbonic acid gas is monatomic, and oxygen bi-atomic); that is to say, 12 At. carbonic acid to 1 At. oxygen. Hence the reaction may perhaps be expressed by the following equation:

$$4R^2Cl^3 + 12(NaO,CO^2) = 12NaCl + 2RO,3R^2O^3 + 12CO^2 + O.$$

### C. Sesquioxide of Rhodium, or Rhodic Oxide. $R^2O^3$.

Metallic rhodium scarcely dissolves in any acid; aqua-regia dissolves it when alloyed with bismuth, lead, copper, or platinum (not when combined with gold or silver). (Wollaston.) It likewise dissolves in fused bisulphate of potash (Berzelius), and in fused hydrate of phosphoric acid (Fischer).

*Preparation.*—1. Pulverulent rhodium is ignited in a silver crucible with hydrate of potash and a small quantity of nitre, whereupon it takes fire, detonates slightly, and swells up to a dark brown mass of rhodiate of potash. This product, after cooling, is well washed with water, which extracts the greater part of the potash and nitre, and the undissolved portion is digested with hydrochloric acid, which, being acted upon by the residual nitric acid, gives off a certain portion of chlorine: in this manner the hydrated oxide is obtained. Continued washing with water may be substituted for the digestion with hydrochloric acid.—2. The aqueous solution of chlororhodiate of potassium or sodium is mixed with excess of carbonate of potash or soda, and evaporated to dryness. The mixture, which is clear at first, gradually becomes gelatinous, by separation of hydrated oxide, the change spreading throughout the whole mass. The hydrate is washed upon a filter, and then dried and ignited. Sometimes a small portion of the oxide remains dissolved in the filtrate and imparts a greenish colour to it, and a small portion of alkali, not removable by water, remains attached both to the hydrated and to the anhydrous oxide. Hydrated rhodic oxide prepared by either of these processes retains its water with great obstinacy, and requires an hour's ignition to render it anhydrous; no oxygen is disengaged by the ignition. (Berzelius.)

This oxide is black.

| | | | |
|---|---|---|---|
| 2R | 104 | | 81·25 |
| 3O | 24 | | 18·75 |
| $R^2O^3$ | 128 | | 100·00 |

($R^2O^3 = 2 \cdot 651{\cdot}387 + 300 = 1602{\cdot}774$. Berzelius.)

The anhydrous oxide and its hydrate are reduced by hydrogen gas, even at ordinary temperatures, the decomposition being accompanied by evolution of heat.

*Combinations.*—*a.* With Water.—Hydrate of Rhodic Oxide.—The preparation has been already described in treating of the anhydrous oxide.—Greenish grey or brown. According to a former statement of Berzelius, the hydrate obtained by the first method is resolved by heating with sulphuric acid into oxygen gas and sulphate of the protoxide.

| | | | Berzelius. |
|---|---|---|---|
| 2R | 104 | 75·91 | 78·60 |
| 3O | 24 | 17·52 | 15·36 |
| HO | 9 | 6·57 | 6·04 |
| $R^2O^3$,HO | 137 | 100·00 | 100·00 |

The hydrate examined by Berzelius retained a small quantity of metallic rhodium.

*b.* With Acids, forming the Salts of Rhodic Oxide, or Rhodic Salts.—These salts are not easily obtained from the metal; they may however be formed: 1. By fusing the metal with bisulphate of potash, sulphurous acid being then gradually evolved.—2. By fusion with hydrated phosphoric acid.—3. By dissolving an alloy of rhodium with bismuth, copper, lead, or platinum, in aqua-regia.—4. By passing chlorine gas over a heated mixture of rhodium and chloride of potassium or sodium, and dissolving the resulting chlorine-salt in water. The anhydrous oxide is not soluble in any acid, but dissolves in melted bisulphate of potash. The hydrate prepared by the first method is insoluble in acids; that obtained by the second dissolves in acids, in conjunction with the potash which adheres to it, producing, however, not a red but a yellow solution. (Berzelius.) The acid solutions of rhodic oxide have, for the most part, a bright rose colour; their taste is purely astringent. Hydrogen gas passed over the anhydrous salts gently heated reduces the rhodium to the metallic state. (Berzelius.) The solutions treated with zinc, iron, copper, and mercury, yield metallic rhodium in the form of a black powder; silver does not produce this effect. (Wollaston.) Tin or the aqueous solution of the protochloride yields with strong solutions a brownish yellow precipitate or a brown solution; with more dilute solutions, it produces a pure yellow precipitate, and with still more dilute solutions (1 pt. of rhodium to 1500 of liquid), merely a yellow colouring. (Fischer, *Schw.* 53, 117.) Protochloride of tin darkens the solution, and, after a while, precipitates the oxide in a state in which it is soluble in acids. (Berzelius.) Green vitriol throws down from hydrochlorate of rhodic oxide and ammonia, a yellow powder, very easily soluble in hydrochloric acid, but exerts no further action. (Fischer.) Hydrosulphuric acid produces—only in warm solutions, according to Berzelius, and only after some time, according to H. Rose—a brown precipitate, soluble in hydrochloric acid, provided the solution contains at least 1 part of rhodium in 2000 parts of liquid. (Fischer.) Hydrosulphate of ammonia, after long standing, or on the application of heat, throws down brown sulphide of rhodium (Descotils), insoluble in excess of the precipitant. (Berzelius.) Caustic ammonia, or carbonate of ammonia, produces, after a while, a lemon-yellow precipitate of rhodiate of ammonia, which dissolves in hydrochloric acid, and forms a yellow solution. (Berzelius.) Potash precipitates, on evaporation, a yellowish brown jelly, consisting of hydrated rhodic oxide containing potash. A similar reaction is produced by carbonate of potash or soda. (Berzelius.) Lime-water added to hydrochlorate of rhodic oxide produces, even in the dark, a pure red-brown precipitate of the hydrated oxide. (Fr. Weiss & Fr. Döbereiner, *Ann. Pharm.* 14, 21, and 253.) Iodide of potassium darkens the solution, and produces, after a while, a slight precipitate. (H. Rose.) No precipitates are produced by phosphate of soda, sal-ammoniac, chloride of potassium, chromate of potash, oxalic acid, cyanide of potassium, cyanide of mercury, ferrocyanide or ferricyanide of potassium, and gallic acid.

## Rhodium and Phosphorus.

Phosphate of Rhodic Oxide, or Rhodic Phosphate.—Formed by boiling pulverulent rhodium with a strong solution of phosphoric acid,—or better, by fusing it with hydrated phosphoric acid, keeping the heat, however, below redness. Microcosmic salt likewise exerts a solvent action, but

less energetic. The solution diluted with water is yellow, the concentrated solution brownish. Potash or soda added to the solution produces no precipitate, but, after continued digestion, separates the neutral rhodium-salt [hydrated oxide?] in the form of a jelly. A similar reaction is produced by ammonia, which, however, likewise changes the yellow colour of the solution into green or blue, according to the concentration and the quantity of free acid. The action is accelerated by a gentle heat; but if the heat be immediately raised to the boiling point, the change of colour does not take place; when, however, the green colouring has once been produced, it is not destroyed by boiling. Nitric acid changes the blue or green colour of the mixture to violet; hydrochloric also acts in a similar manner, but only when aided by gentle heat; at a higher temperature, the liquid regains its yellow colour. (Fischer, *Pogg.* 18, 257.)

## Rhodium and Sulphur.

A. Protosulphide of Rhodium.—1. Rhodium heated in sulphur-vapour takes up the sulphur, with incandescence. (Berzelius.)—2. The sulphide is also formed by heating to whiteness a mixture of chlororhodiate of ammonia and an equal weight of sulphur. (Vauquelin.)—3. By precipitating aqueous chlororhodiate of sodium with hydrosulphuric acid, washing the precipitate in boiling water, and freeing it from water [and part of the sulphur?] by ignition in a stream of carbonic acid gas. (Fellenberg, *Pogg.* 50, 63.) Fused, bluish white, metallic mass. When heated in the air, it gives off sulphurous acid, and throws out numerous rough vegetations, till the metal is left behind in the form of a white, spongy, friable mass. (Vauquelin.) The sulphide prepared by the third method, when heated in a current of dry chlorine gas, yields chloride of sulphur and protochloride of rhodium. (Fellenberg.)

| | | | Vauquelin (2). | Fellenberg (3). |
|---|---|---|---|---|
| R | 52 | 76·47 | 79·36 | 76·52 |
| S | 16 | 23·53 | 20·64 | 23·48 |
| RS | 68 | 100·00 | 100·00 | 100·00 |

B. Sesquisulphide of Rhodium.—Chlororhodiate of sodium forms with hydrosulphate of ammonia, on the application of heat, a dark brown precipitate, which turns acid when exposed to the air, in the same manner as the similarly formed sulphide of platinum, though less quickly; it dissolves completely in hydrosulphate of potash, partially in caustic potash, with separation of rhodium and formation of hyposulphurous acid. (Berzelius.) Nitric acid dissolves it, and forms a brown solution. (Descotils.)

C. Sulphate of Rhodious Oxide, or Rhodious Sulphate.—Formed by heating rhodic sulphate to redness; by gently heating sulphide of rhodium in contact with air; or by heating the hydrate of rhodic oxide with sulphuric acid. Black powder, insoluble in water and acids; potash extracts from it the half of its sulphuric acid. (Berzelius.)

D. Sulphate of Rhodic Oxide, or Rhodic Sulphate.—Prepared by heating sesquisulphide of rhodium with fuming nitric acid, evaporating the liquid, and decanting it from the separated powder. Part of it remains

dissolved in the decanted nitric acid, and imparts to it a yellowish brown colour. Black-brown powder, which absorbs moisture from the air, and turns red; it dissolves easily in water. The reddish yellow or dark red solution yields, on evaporation, not a powder, but a brown syrup; and if the heat be continued, this residue swells up to a spongy mass, which dissolves very slowly but completely in water, deliquesces more quickly in the air, and, when more strongly heated, gives off sulphuric acid and oxygen gas, and is converted into the preceding salt C. (Berzelius.) If the aqueous solution be precipitated by chloride of barium, the filtrate contains sesquichloride of rhodium. The precipitated sulphate of baryta appears brownish yellow, from admixture of a large quantity of rhodic oxide, the greater part of which may, however, be extracted by boiling hydrochloric acid.

## Rhodium and Chlorine.

A. Protochloride of Rhodium.—1. Formed by decomposing $\frac{5}{4}$-chloride of rhodium with boiling potash, and heating the brownish grey precipitate of rhodioso-rhodic oxide with hydrochloric acid, which forms a red solution of sesquichloride of rhodium and leaves the protochloride undissolved. (Berzelius.)—2. When dry chlorine gas is passed over heated protosulphide of rhodium, 100 parts of protosulphide yield 128·4 parts of protochloride. (Fellenberg.)—By (1): Greyish red or dingy violet powder which bakes together in drying. (Berzelius.)—By (2): Of a fine rose-red colour. (Fellenberg.)—Sustains a gentle heat without decomposition, but when heated in hydrogen gas, it is resolved into hydrochloric acid and 60 per cent. of rhodium. (Berzelius.) The metal thus reduced has a pure white colour. (Fellenberg.)—Chloride of rhodium is not altered by continued heating in a stream of chlorine gas. It likewise resists the action of caustic potash or carbonate of potash at a boiling heat, and is insoluble in water, hydrochloric acid, and nitric acid. (Fellenberg.)

| | | | | | Berzelius (1). | | Fellenberg (2). |
|---|---|---|---|---|---|---|---|
| R | 52·0 | .... | 59·50 | ..... | 60 | .... | 59·49 |
| Cl | 35·5 | .... | 40·50 | ..... | 40 | .... | 40·51 |
| RCl | 87·4 | .... | 100·00 | ..... | 100 | .... | 100·00 |

B. Five-fourths Chloride of Rhodium.—To form this compound, finely divided rhodium, as obtained by reducing chlororhodiate of potassium or sodium with hydrogen gas, is gently ignited, and chlorine passed over it, till it ceases to increase in weight. The metal when thus treated, increases in bulk, and is converted into the $\frac{5}{4}$-chloride. At the same time, three sublimates, small in quantity, are formed, viz., ($\alpha$), at the greatest distance from the heated part, a yellow substance which forms a yellow solution in water; ($\beta$), in the middle, a dark red, non-crystalline sublimate of sesquichloride of rhodium; and ($\gamma$), nearest to the heated part, a thin, light grey deposit, insoluble in water and acids, and decomposed by alkalis, with separation of brownish yellow hydrate of rhodic oxide. 100 parts of rhodium, by thus absorbing chlorine, increase by 84·25 parts, including the three sublimates.

Pale, rose-coloured powder, insoluble in water and hydrochloric acid, not affected by cold potash, but decomposed by boiling potash, with separation of gelatinous, yellowish brown-grey hydrate of rhodioso-rhodic oxide. (Berzelius.)

| | | | | Berzelius. |
|---|---|---|---|---|
| 4R | 208 | 54·03 | | 54·27 |
| 5Cl | 177 | 45·97 | | 45 73 |
| $2RCl,R^2Cl^3$ | 385 | 100·00 | | 100·00 |

C. Sesquichloride of Rhodium.—Formed by dissolving chlororhodiate of potassium in water—precipitating the potash by hydrofluosilicic acid not in excess—filtering—evaporating—dissolving the residue in water, which leaves behind a small quantity of silico-fluoride of potassium—and once more evaporating the solution, with addition of concentrated hydrochloric acid, in order to drive off the obstinately adhering fluoride of silicium. Black-brown, non-crystalline.—Sustains a strong heat before it gives off its chlorine, and by a stronger heat, is immediately resolved into chlorine gas and metallic rhodium. When exposed to the air, it gradually softens and deliquesces. (Berzelius.)

| | | | |
|---|---|---|---|
| 2R | 104·0 | | 49·48 |
| 3Cl | 106·2 | | 50·52 |
| $R^2Cl^3$ | 210·2 | | 100·00 |

*Aqueous Sesquichloride of Rhodium*, or *Hydrochlorate of Rhodic Oxide.*—Sesquichloride of rhodium dissolves in water, forming a rose-coloured solution which does not yield crystals on evaporation. (Wollaston, Berzelius.) The solution in aqueous hydrochloric acid is yellow, and does not recover its red-colour till the excess of acid has been expelled by evaporation. (Berzelius.)—The salt likewise dissolves in alcohol, forming a rose-coloured solution. (Wollaston.)

## Rhodium and Nitrogen.

A. Nitrate of Rhodic Oxide, or Rhodic Nitrate.—The solution of the hydrated sesquioxide in nitric acid, is red, not crystallizable, and is precipitated by copper and mercury, but not by silver. (Wollaston.) By treating with nitric acid the hydrated oxide containing potash, obtained by the second method (p. 360), a solution is obtained which has a pure yellow colour, and dries up to a yellow syrup. (Berzelius.)

B. Rhodiate of Ammonia.—Aqueous chlororhodiate of sodium supersaturated with ammonia, gives no precipitate at first, but assumes a paler red colour, then turns yellow, and afterwards deposits lemon-yellow hydrated rhodiate of ammonia, which dries up to a powder of a paler yellow colour. This, when heated in a retort, gives off water and nitrogen without any noise, and leaves metallic rhodium. It readily dissolves in hydrochloric acid, forming a lemon-yellow solution, which retains its colour unaltered during evaporation, and does not turn red till it dries up. (Berzelius.)

C. *Ammonio-sesquichloride of Rhodium ?*—The aqueous solution of the following compound D, deposits a greyish yellow powder on the addition of ammonia. Part of the product, however, remains dissolved in the excess of ammonia, and is obtained by evaporating the filtered liquid to dryness and digesting the residue with a small quantity of water. The greyish yellow powder gives off sal-ammoniac vapour when heated, and is slightly soluble in water. (Vauquelin.)—2. When rhodiate

of ammonia has been precipitated by ammonia from the solution of chlororhodiate of sodium, the yellow liquid decanted from it, deposits, on cooling, a yellow salt, which is for the most part insoluble in water. This salt, if heated in a retort, after being washed and dried, gives off nitrogen gas, water, hydrochloric acid, sal-ammoniac, and metal. (Berzelius.)

D. Chlororhodiate of Ammonium.—*Preparation* (p. 257, No. 15). To purify it further, the salt, which is insoluble in alcohol of 36° Bm. may be dissolved in water, which will leave behind a yellow powder, apparently containing platinum, lead, and iron; the solution is then to be evaporated to dryness, and the pulverized residue repeatedly exhausted with alcohol, first of 36° and then of 40° Bm., which extracts the excess of sal-ammoniac. The residue is redissolved in water and crystallized. (Vauquelin.)—Long, blackish red, very brilliant, four-sided prisms, which exhibit a garnet colour by transmitted light, yield a fine red powder, and when heated, leave 0·31 rhodium. (Vauquelin. *Ann. Chim.* 93, 204.) Without the purification just described, Vauquelin formerly obtained ruby-coloured, very brilliant, six-sided laminæ, which, when heated, left from 0·28 to 0·29 of metal. The salt dissolves readily in water, forming a red solution; bichloride of platinum added to the solution throws down chloroplatinate of ammonium, while hydrochlorate of rhodic oxide remains in solution. It is insoluble in alcohol. (Wollaston.)

| | *Crystallized.* | | | Vauquelin. |
|---|---|---|---|---|
| $2NH^4Cl$ | 106·8 | .... | 31·89 | |
| 2R | 104·0 | .... | 31·04 | ..... 31 |
| 3Cl | 106·2 | .... | 31·70 | |
| 2HO | 18·0 | .... | 5·37 | |
| $2NH^4Cl,R^2Cl^3+2Aq.$ | 335·0 | .... | 100·00 | |

## Rhodium and Potassium.

A. Rhodioso-rhodiate of Potash.—The hydrate of $2RO,R^2O^3$ dissolves in excess of potash, forming a yellow solution, from which it may be precipitated by hydrochloric acid. (Berzelius.)

B. Rhodiate of Potash.—*a.* The mass obtained by igniting rhodium-dust in a silver crucible with hydrate of potash and a small quantity of nitre, leaves, when washed with cold water, a light, flea-brown powder containing from 15 to 16 per cent. of potash, which may be dissolved out by nitric or sulphuric acid. (Berzelius.)—The hydrated oxide precipitated by potash from a solution of chlororhodiate of sodium dissolves in excess of the potash, forming a yellow solution. (Descotils, *A. Gehl.* 6, 431.)

C. Sulphorhodiate of Potassium.—Sesquisulphide of rhodium obtained by precipitation with hydrosulphuric acid, dissolves in aqueous sulphide of potassium. (Berzelius.)

D. Sulphate of Rhodic Oxide and Potash.—An aqueous mixture of chlororhodiate of potassium and sulphurous acid, left to itself for a while, deposits a powder, which is yellowish white at first, but white after washing and drying, and contains $KO,SO^3+R^2O^3,3SO^3$.—This powder, when distilled, gives off sulphurous acid and oxygen gas, and leaves

34·7 per cent. of rhodic oxide mixed with sulphate of potash; when ignited in hydrogen gas, it yields 28 per cent. of metal. It dissolves very sparingly in water, imparting a yellow colour, and somewhat more freely in sulphuric acid, which it colours lemon-yellow; when decomposed by boiling potash, it yields a lemon-yellow hydrate of rhodic oxide. (Berzelius.)—The rhodium deoxidized by this formation of sulphuric acid, is found in the liquid below. This liquid mixed with carbonate of soda and evaporated, deposits a gelatinous, deep yellowish green hydrate of the protoxide, which dissolves in nitric acid, with separation of metallic rhodium, and forms a yellowish green solution. The liquid filtered from the hydrated protoxide is pale green, but becomes red again when evaporated with hydrochloric acid. (Berzelius.)

*b.* Metallic rhodium and rhodic oxide dissolve slowly when fused with bisulphate of potash in a covered crucible at a dull red heat, the action in the former case being attended with evolution of sulphurous acid. The mass, when cold, may be mixed with oil of vitriol and fused again. The fused mass, if it contains but little rhodic oxide, is red and transparent; but a larger quantity renders it black and opaque; when solidified, it is light or dark yellow, or sometimes rose-coloured. It dissolves slowly in cold water, quickly in boiling water, forming yellow solutions. The solution is imperfectly precipitated by sulphuretted hydrogen and by alkalis; and on mixing it with excess of carbonate of potash or soda, evaporating to dryness, igniting the residue in a platinum crucible, and exhausting, first with water, and afterwards with hydrochloric acid, the whole of the oxide remains undissolved. (Berzelius.)

E. Chlororhodiate of Potassium.—1. Finely pulverized rhodium intimately mixed with an equal weight of chloride of potassium, and heated to dull redness in a glass tube through which chlorine gas is passed for two hours, till it is no longer absorbed, forms a closely aggregated, red-black mass. This substance is dissolved in water—the solution filtered to separate the rhodium which still remains metallic—then mixed with alcohol—and the resulting red precipitate washed with alcohol of specific gravity 0·840, to dissolve out all the free chloride of potassium. The alcoholic solution remains red, and, on evaporation, deposits the greater part of the rhodium in the metallic state. (Berzelius.)—If the solution containing platinum and rhodium, obtained in the analysis of platinum ore (p. 257, No. 10,) be mixed with excess of chloride of potassium instead of common salt, and the liquid decanted from the precipitated chloroplatinate of potassium be left to evaporate freely, the remainder of the chloroplatinate of potassium separates out first, and afterwards the chlororhodiate. (Berzelius.)

Dark red, rectangular prisms, with four-sided summits. They do not give off their water of crystallization till heated above 100°. (Berzelius.)

| | *Dried.* | | | Berzelius. |
|---|---|---|---|---|
| 2KCl | 149·2 | 41·51 | | 41·54 |
| 2R | 104·0 | 28·94 | | 28·98 |
| 3Cl | 106·2 | 29·55 | | 29·48 |
| $2KCl,R^2Cl^3$ | 359·4 | 100·00 | | 100·00 |

| | *Crystallized.* | | Berzelius. |
|---|---|---|---|
| 2KCl | 149·2 | 39·53 | |
| $R^2Cl^3$ | 210·2 | 55·70 | |
| 2HO | 18·0 | 4·77 | 4·88 |
| $2KCl,R^2Cl^3+2Aq.$ | 377·4 | 100·00 | |

When chlororhodiate of ammonium is mixed with an excess of potash, ammonia is evolved, and a rose-coloured precipitate is formed, which gradually disappears again, especially on the application of heat, while the liquid acquires a greenish yellow colour, and on exposure to the air, deposits greyish yellow crystals insoluble in alcohol. If the excess of potash be removed from the liquid by hydrochloric acid, yellowish white flakes are deposited, slightly soluble in water.

### Rhodium and Sodium.

A. Rhodiate of Soda.—Aqueous caustic soda dissolves rhodic oxide with a yellow colour. (Descotils.)

B. Chlororhodiate of Sodium.—*Preparation.* 1. Similar to the first method for the potassium-salt, 1 part of rhodium, however, requiring 2 parts of chloride of sodium. (Berzelius.)—2. In the analysis of platinum ore (p. 257, No. 10). (Wollaston.)—Crystallizes combined with water, in rhombic prisms whose acute dihedral angles measure 75° (Wollaston); in octohedrons. (Descotils.) The crystals have a fine red colour and taste like common salt. In dry air, they effloresce and are converted into a peach-blossom-coloured powder, and fuse in their water of crystallization when heated. (Descotils. *A. Gehl.* 6, 430.) They then give off 30 per cent. of water; but the last portion does not escape till they are heated nearly to redness in a current of dry chlorine gas. (Berzelius.) After strong ignition, there remains a mixture of rhodium and chloride of sodium. (Descotils.)—The crystals dissolve in $1\frac{1}{2}$ pt. of water, forming a cochineal-coloured solution; they are not soluble in alcohol. (Wollaston.)

| | *Crystallized.* | | | Berzelius. |
|---|---|---|---|---|
| 3NaCl | 175·6 | .... | 45·52 | ..... 45·57 |
| 2R | 104·0 | .... | 26·95 | ..... 27·10 |
| 3Cl | 106·2 | .... | 27·53 | ..... 27·33 |
| $3NaCl,R^2Cl^3$ | 385·8 | .... | 100·00 | ..... 100·00 |

Analyses giving different results have been made by Thomson (*Schw.* 47, 62,) and Biewend (*J. pr. Chem.* 15, 126).

C. Nitrate of Rhodic Oxide and Soda.—Dark red crystals, easily soluble in water, but insoluble in alcohol. (Berzelius.)

### Rhodium and Calcium.

Rhodiate of Lime.—Formed when the potash or nitre with which the metal is ignited contains lime. (Berzelius.)

Alumina exhibits similar relations with rhodium.

### Rhodium and Arsenic.

A. Arsenide of Rhodium.—The alloy obtained by fusing the two metals together, gives off arsenic when heated to redness in the air, while brittle rhodium remains behind. (Wollaston.)

B. Arseniate of soda produces a yellowish white precipitate with chlororhodiate of sodium, but only when heated. (Thomson.)

### Rhodium and Bismuth.

Alloy.—1 part of rhodium forms with 3 parts of bismuth, an alloy which is wholly soluble in aqua-regia.

### Rhodium and Lead.

Alloys.—1 part of rhodium and 2 parts of lead form an alloy which has a density of 11·3.—The alloy of 1 pt. rhodium and 3 lead is perfectly soluble in aqua-regia. (Wollaston.)

### Rhodium and Iron.

Carbide of Rhodium and Iron.—*a.* 1 pt. rhodium to 1 steel: sp. gr. 9·176; has a very fine colour and surface for metallic mirrors, and does not tarnish in the air.—*b.* 1 pt. rhodium with 50 to 100 steel: Very hard and tolerably tough alloy, which requires to temper it, a higher temperature by 39° than common steel, and 17° higher than Indian steel. (Faraday & Stodart, *Gilb.* 66, 167.)

### Rhodium and Copper.

Alloy.—1 pt. rhodium and 3 pts. copper form an alloy which dissolves completely in aqua-regia.

### Rhodium and Silver.

Alloy.—A very malleable and fusible alloy, which, when slowly cooled after fusion, becomes covered with a black powder (of protoxide of rhodium, according to Berzelius). In these compounds, the rhodium is not attacked by aqua-regia. (Wollaston.)

### Rhodium and Gold.

Alloys.—*a.* 1 pt. rhodium with 4 to 5 gold. Very malleable and difficultly fusible alloy, the colour of which cannot be distinguished from that of pure gold; when slowly cooled after fusion, it becomes covered with a black powder.—*b.* 1 pt. rhodium to 6 gold: More fusible than *a*, but less fusible than gold.—In these compounds, the rhodium is not attacked by aqua-regia. (Wollaston.)

## Chapter XLIII.

# IRIDIUM.

*Besides the Memoirs cited on page 252:*

Tennant. *Phil. Trans.* 1804, 411; also *A. Gehl.* 5, 166.
Descotils. *Ann. Chim.* 48, 153; also *A. Gehl.* 2, 73.
Fourcroy & Vauquelin. *Ann. Chim.* 50, 5; also *A. Gehl.* 3, 262.
Vauquelin. *Ann. Chim.* 89, 150 and 225; also *Schw.* 24, 21.
Berzelius. *Pogg.* 13, 463; 15, 208 and 527.
Claus. *Ann. Pharm.* 59, 234; 63, 341.

*History.* Descotils, as well as Fourcroy & Vauquelin, pointed out the existence of the two metals contained in the insoluble part of platinum ore, but regarded them as identical. Tennant, however, soon after showed, in 1804, that this insoluble residue really contained two distinct metals, Iridium and Osmium, and the chemical relations of these metals have been most minutely examined by Berzelius. Claus has since demonstrated (in 1845) the existence of another metal, Ruthenium, in this residue, and has shown that many of the properties hitherto ascribed to iridium really belong to a mixture of iridium and ruthenium.

*Sources.* 1. In platinum ore, in small quantity, alloyed with platinum and other metals (p. 254).—2. As Osmide of iridium, mixed with the platinum ore in separate grains.—3. As the so-called *Native Iridium* (*vid. Alloy of Platinum and Iridium*).—4. In the state of oxide, together with the oxides of osmium, iron, and chromium (in *Irite*).

*Preparation.* pp. 258, 259, No. 18—25; p. 262, No. 23—27; p. 265, No. 27; pp. 268, 269, No. 1—4; p. 270, No. 1—6.

It is difficult to obtain iridium free from osmium, which obstinately adheres to it. The presence of osmium is discovered by the luminosity which it imparts to the flame of a spirit-lamp, when a sample of the metal is laid on the edge of a piece of platinum foil and held in the outermost border of the flame (II. 30). If the foil be then held in the middle of the flame, the iridium will be brought back to the metallic state, and if it be then again held in the edge of the flame, the luminosity will be again increased. Osmium is best removed by igniting the iridium in a current of chlorine gas, which carries away the chloride of osmium, and leaves pure protochloride of iridium, reducible either by moderate ignition in an atmosphere of hydrogen, or by intense ignition *per se*.

*Properties.* Remains in the form of a grey powder when iridium sal-ammoniac is heated to redness.—By reduction with hydrogen, it is obtained in the form of a mass resembling platinum, and having a specific

gravity of 15·8629. (Berzelius.)—When sesquioxide of iridium is prepared by igniting chloriridiate of potassium with excess of carbonate of potash (p. 265, No. 27); then washed with water and hydrochloric acid; strongly pressed between bibulous paper, till half dry; afterwards completely dried without pressure; and the coherent mass exposed to a white heat for half an hour in a covered crucible,—the iridium remains in the form of a coherent mass, which has a similar appearance to platinum; is difficult to break, but crumbles under the hammer, and may be reduced to powder by trituration; takes a polish when gently pressed with the burnisher; has a specific gravity of 15·588; and when heated in an ether-flame fed with oxygen gas, does not fuse, but acquires a more silvery whiteness. (Berzelius.) Vauquelin fused it in very small quantity only on charcoal ignited in a stream of oxygen, and obtained a somewhat ductile globule. Children (*Schw.* 16, 365) fused it by his galvanic battery into a white, strongly lustrous, brittle, and still somewhat porous globule: of specific gravity 18·68. This globule probably contained platinum. (Berzelius.)—1 gramme of iridium heated upon charcoal before Döbler's oxy-hydrogen blowpipe, fuses into a bright globule, which, however, appears to absorb gas, since, on solidifying, it throws out excrescences, and cavities are formed in its interior. In colour it is intermediate between silver and tin; it is somewhat crystalline, of specific gravity 15·93, harder than iron, and so brittle that when struck with a hammer it flies into small pieces having a fine-grained fracture. (Bunsen, *Pogg.* 41, 207). When reduced in this manner, the iridium may have taken up silicium from the charcoal. (Berzelius).

*Iridium-black.*—When an alcoholic solution of iridic sulphate is heated for some time, a black powder is obtained, which is similar to platinum-black, and converts alcohol into acetic acid, but does not become red-hot in alcohol vapour. If, on the contrary, the mixture of iridic sulphate and alcohol be exposed to sunshine at ordinary temperatures, and the separated black powder heated with a large quantity of water nearly to the boiling point, and then dried at 100°, it acquires the power of exciting combustion in a much higher degree than platinum-black. The smallest particles of this iridium-black thrown upon paper moistened with alcohol produce a hissing noise, become red-hot, and acquire the grey colour of ignited iridium. (W. Döbereiner, *Schw.* 63, 465.)—By digesting sesquichloride or sesquioxide of iridium with formic acid, an iridium-black is likewise obtained, very easily soluble in aqua-regia. (Berzelius, *Lehrbuch.*)

When a solution of bisulphide of iridium in aqua-regia is evaporated to the consistence of a syrup, the residue mixed with twice its weight of alcohol of 80 per cent., the mixture spread upon glass, and the glass heated to redness, there remains a smooth specular coating of iridium, which likewise exhibits inflaming power. (Böttger, *J. pr. Chem.* 3, 276.)

Pulverulent iridium is the best adapted of all substances for producing a pure black upon porcelain. (Frick, *Pogg.* 31, 17.)

## *Compounds of Iridium.*

### Iridium and Oxygen.

When iridium, which has not been brought into the white compact state by exposure to a white heat, is ignited alone in the air, or with

hydrate of potash in a vessel to which the air has access, or with hydrate of potash and nitre, it oxidizes and is converted into sesquioxide. When pure, it is but very slightly soluble in aqua-regia; but when alloyed with platinum, it dissolves freely, and is converted into hydrochlorate of iridic oxide. Pure iridium does not dissolve in oil of vitriol, nitric acid, or melted bisulphate of potash; the latter, however, converts it into sesquioxide.

A. Protoxide of Iridium, or Iridious Oxide.—IrO.—1. Formed by boiling the protochloride prepared in the dry way with tolerably strong potash. The protoxide then separates in the form of a heavy black powder, which must be washed and treated with an acid to free it from potash. The potash retains a certain quantity of the protoxide in solution, and the liquid, when exposed to the air, gradually absorbs oxygen, and acquires first a purple-red and then a dark blue colour.—2. By gently igniting the hydrate. (Berzelius.)

| | | | |
|---|---|---|---|
| Ir ..... | 99 | ..... | 92·52 |
| O ..... | 8 | ..... | 7·48 |
| IrO ..... | 107 | ..... | 100·00 |

(IrO = 1233·499 + 100 = 1333·499. Berzelius.)

*Combinations.—a.* With Water.—Hydrated Iridious Oxide.—1. Formed by treating the aqueous solution of protochloride of iridium and potassium or sodium, with carbonate of potash or soda, taking care however to add only a very slight excess, as otherwise the hydrate will redissolve and form a greenish yellow solution. (Berzelius.)

*b.* With Acids, forming the Salts of Iridious Oxide, or Iridious Salts.—The anhydrous oxide dissolves very sparingly in boiling acids, the hydrate more freely. The solution has a dingy green or greenish brown colour; in the dilute state, it is colourless. (Berzelius.) With chlorine it passes to a higher state of oxidation and becomes blue or red-brown. (Berzelius.)

*c.* With potash.

*Blue Oxide of Iridium.*—This oxide must be regarded as a mixture of the oxide and sesquioxide.—It is sometimes produced when iridium is ignited with hydrate of potash in a covered crucible, or when chloriridiate of sodium is fused with iridium,—likewise by partial deoxidation of solutions of the sesquioxide, and by boiling the protochloride with excess of potash, which then acquires a blue or purple colour on exposure to the air. The surest method of obtaining it, is to supersaturate the aqueous solution of chloriridiate of potassium or sodium with ammonia, and evaporate till it retains only a slight odour of ammonia; it then turns blue and deposits the blue oxide, which must be collected on a filter just at the proper time, as it would disappear again during the evaporation of the liquid to dryness, and leave ammonio-protochloride of iridium. The liquid runs through colourless at first, but the wash-water acquires a pale blue tint by taking up a small quantity of the blue oxide. The oxide thus obtained—which contains ammonia, and therefore, when heated, is reduced with violent decrepitation and often with detonation—dissolves in acids, especially in hydrochloric acid, and forms a dark blue solution. (Berzelius.)—By igniting iridium with hydrate of potash and nitre, or simply with hydrate of potash in a vessel to which the air has access, a compound

of the blue oxide with potash is obtained. Acids dissolve it and form blue solutions, which are decolorized by zinc, tin, iron, protochloride of tin, green vitriol, and hydrosulphuric acid; a small quantity of chlorine restores the blue colour, and a larger quantity colours the solutions purple-red; but this colour again gives place to the blue, when the liquid is exposed to the air. By continued boiling, the blue solutions become green, then violet, then purple, and are ultimately converted into the brown-red salts of iridic oxide. The blue salts are not precipitated by potash or ammonia; if, however, they contain titanic or ferric oxide, these substances are precipitated in combination with a small quantity of blue oxide. (Vauquelin.)—According to Claus, this blue oxide is in reality the bioxide, $IrO^2$. (see page 374).

B. Sesquioxide of Iridium.—$Ir^2O^3$.—*Formation.* 1. The finely divided metal is quickly converted into sesquioxide by ignition in the air; the compact metal more slowly; at a stronger heat, the metal is reduced.—2. When iridium is ignited with hydrate or carbonate of potash, either in contact with the air or mixed with nitre, a compound of the sesquioxide with potash is produced. The sesquioxide combines with the potash, but separates out for the most part when the mixture is dissolved in water, because the aqueous potash retains less of it in solution; if only a moderate heat be applied, or if the quantity of potash be too small, iridium and the protoxide remain mixed with the product.—3. Iridium fused with bisulphate of potash, is converted into sesquioxide, but is not dissolved. (Berzelius.)

*Preparation.* Chloriridiate of potassium is mixed with twice its weight of carbonate of potash or soda, and the mixture heated in a covered silver or porcelain crucible, till the bottom exhibits a dull red heat.—In this case, a mixture of 1 vol. oxygen and 8 vol. carbonic acid gas is evolved:

$2IrCl^2 + 4(NaO, CO^2) = Ir^2O^3 + 4NaCl + O + 4CO^2$; and 1 At. O : 4 At. $CO^2$ = 1 vol. O : 8 vol. $CO^2$. If too much heat be applied, the sesquioxide drives out the carbonic acid and unites with alkali, forming a compound which dissolves with yellow colour in water.—The saline mass is dissolved in boiling water, which does not dissolve any of the iridium, and the sesquioxide washed on the filter with water containing sal-ammoniac (if pure water be used, it runs through the filter in the form of a greenish blue, turbid liquid), after which the sal-ammoniac is removed by heat, and the still adhering alkali by an acid. (Berzelius.)

Soft, bluish black powder. (Berzelius.)

| | | | |
|---|---|---|---|
| 2Ir | 198 | .... | 89·19 |
| 3O | 24 | .... | 10·81 |
| $Ir^2O^3$ | 222 | .... | 100·00 |

($Ir^2O^3 = 2 \cdot 1233{\cdot}499 + 300 = 2766{\cdot}998$. Berzelius.)

Sustains a red heat without decomposition, but when heated above the melting point of silver, it is resolved into metallic iridium and oxygen. Hydrogen gas, even at ordinary temperatures, reduces it to the metallic state, the decomposition being attended with rise of temperature (amounting even to ignition according to Wöhler); it is likewise reduced with strong detonation when mixed with a combustible body and heated. (Berzelius.)

*Compounds.*—*a.* With water.—Hydrated Sesquioxide of Iridium. —Formed when an aqueous solution of sesquichloride of iridium or its compound with chloride of potassium or chloride of sodium, is treated with potash or soda. Sometimes, however, from some unknown cause, no precipitate is formed even on heating the mixture. The dark brown bulky precipitate contains alkali, which cannot be extracted by water.—Bichloride of iridium and potassium likewise yields, when boiled with aqueous carbonate of potash or soda, a black precipitate, which exhibits all the properties of [hydrated?] sesquioxide of iridium, and dissolves in hydrochloric acid forming a dark brown solution.

¶ The sesquioxide has hitherto been considered as the most important and the most easily prepared of all the oxides of iridium. According to Claus, however, (*Ann. Pharm.* 59, 251,) it can only be obtained under particular circumstances. On treating a solution of sesquichloride of iridium with potash, no precipitate is at first produced; but on heating the liquid for some time, it assumes an indigo colour and then deposits a dark blue hydrate of the *bioxide*, $IrO^2+2Aq$. oxygen being at the same time absorbed from the air. This absorption may be made evident by introducing a solution of sesquichloride of iridium and potassium mixed with a small quantity of potash, into a tube half filled with oxygen gas and closed at the bottom with mercury. After a while, a deep violet-blue colour appears in the liquid, commencing at the top, gradually extending downwards, and becoming continually darker, the liquid at the same time absorbing the gas, rising in the tube, and finally depositing the blue bioxide of iridium in considerable quantity. It would appear from this, that the lower oxides of iridium cannot be prepared in the moist way.—The anhydrous sesquioxide may, however, be obtained by gently igniting a mixture of the sesquichloride of iridium and potassium with carbonate of soda in an atmosphere of carbonic acid; on treating the product with water, the sesquioxide remains in the form of a black powder insoluble in acids. This oxide likewise forms a soluble, pale greenish hydrate; but it is difficult to obtain, because it rapidly absorbs oxygen and is converted into the hydrated bioxide. (Claus.) ¶

*b.* With acids, forming the Salts of Sesquioxide of Iridium.—The anhydrous oxide is insoluble in acids and even in fused bisulphate of potash; the hydrate, however, dissolves in acids, forming solutions of a dark brown or dingy purple-red colour. (Berzelius.)

*c.* With ammonia, potash, and soda.

C. Bioxide of Iridium, or Iridic Oxide.—$IrO^2$.—According to Berzelius and others, this oxide is known only in its salts, and cannot be precipitated by alkalis or alkaline carbonates, because they dissolve it. When a solution of bichloride of iridium and potassium is boiled with carbonate of potash or soda, carbonic acid escapes with effervescence and a precipitate is formed consisting, not of bioxide, but of the black sesquioxide. (Berzelius.)—¶ According to Claus, on the contrary, the bioxide is the most easily prepared of all the oxides of iridium, and is always deposited in the form of a bulky, indigo coloured precipitate, when a solution of either of the chlorides of iridium is boiled with an alkali. The precipitate is a hydrate containing 2 At. water : $IrO^2+2Aq$. It always retains 3 or 4 per cent. of alkali, even after the most careful washing. When deprived of its water by heat, it contains 14 per cent. of oxygen.

| *Anhydrous.* | | | *Hydrated.* | |
|---|---|---|---|---|
| Ir | 99 | 86·09 | Ir | 99 |
| 2O | 16 | 13·91 | 2O | 16 |
| | | | 2HO | 18 |
| $IrO^2$ | 115 | 100·00 | + 2Aq. | 133 |

The hydrate, when heated in an atmosphere of carbonic acid, exhibits a strong momentary incandescence, at the same time giving off all its water, together with 1 or $1\frac{1}{2}$ per cent. of oxygen, and becoming black and insoluble in acids. It is almost insoluble in dilute sulphuric and nitric acid; hydrochloric acid dissolves it slowly but completely, forming a solution which is indigo-coloured at first, but afterwards becomes chrome-green, and finally red-brown when heated, being at the same time converted into bichloride of iridium. This oxide is identical with the blue oxide described on page 371, and hitherto regarded as a compound of protoxide and sesquioxide. (Claus, *Ann. Pharm.* 59, 252.) ¶

The salts of iridic oxide are produced from the salts of the lower oxides by boiling the solutions of the latter in open vessels or with nitric acid. The anhydrous salts are black, and yield red powders; the aqueous solutions are dark brown, red, and almost opaque when concentrated, but reddish yellow when dilute; they impart a distinct yellow colour to large quantities of water.—When evaporated and ignited, they leave metallic iridium. They are decolorized—or in case of great concentration, turned yellowish or pale green—by the following substances, which, for the most part, reduce them to proto-salts; a small quantity of chlorine subsequently added turns them green, and a larger quantity, violet-red. (Vauquelin.) Zinc, tin, iron, and most of the metals—not, however, gold or platinum—decolorize the solutions, and throw down part of the iridium in the form of a black powder. (Tennant.)—Sulphuretted hydrogen decolorizes them at first, and, after a while, forms a brown precipitate of sulphide of iridium; so likewise does hydrosulphate of ammonia, an excess of which, however, easily redissolves the precipitate. (H. Rose.)—Iodide of potassium exerts a decolorizing action. (H. Rose.)—Protochloride of tin decolorizes the solution (Tennant); and forms a pale brown precipitate. (H. Rose.)—Green vitriol decolorizes the solutions (Vauquelin), and forms a dingy green precipitate according to H. Rose, or white, according to Fischer.—Mercurous nitrate produces a pale brown precipitate. (H. Rose.)—Oxalic acid decolorizes the solutions after a while (H. Rose); tincture of galls and cyanide of potassium, immediately (Tennant); so likewise does ferrocyanide of potassium. (H. Rose, *Analyt. Chem.*) According to Fischer, on the contrary (*Schw.* 53, 117), ferrocyanide of sodium and gallic acid exert no particular action.—Ammonia decolorizes the solution and forms a brown precipitate; a portion of the oxide however remains dissolved, without imparting any colour to the liquid. (Vauquelin, H. Rose.) Tennant alone ascribes a purple-red colour to the mixture. If the greater part of the free ammonia be left to evaporate in the air or driven off by boiling, the colourless liquid turns blue and deposits a blue powder. (H. Rose.)—Potash in excess produces a very scanty blackish grey precipitate; the supernatant liquid, which is either colourless or very pale-green, undergoes but little change of colour when heated; but if afterwards set aside, it assumes a continually darker violet-blue colour, the change proceeding from above downwards; if it be then evaporated, it yields a blue precipitate and ultimately a greenish white, dry residue, which when digested in water, forms a colourless solution

and deposits a blue powder. (H. Rose.) [Is the reduction which takes place on the addition of potash or carbonate of potash, due to organic matter derived from the filter?] Carbonate of soda decolorizes the solution after a while, but without producing a precipitate. (H. Rose.)—Neutral carbonate of potash forms with hydrochlorate of iridic oxide, a deep red-brown precipitate, which, however, gradually redissolves, leaving only a trace of black-brown powder. The colourless solution thus formed does not become blue on standing; but if evaporated to dryness, and then treated with water, it yields a small quantity of blue powder, and the liquid turns blue after a while. (H. Rose.)—Bicarbonate of potash, as well as phosphate of soda, decolorizes iridic salts after a while, but without producing a precipitate. (H. Rose.) Nitrate of silver produces a deep indigo-coloured precipitate, which becomes colourless after a while (see p. 392).

The mixing of iridic with iridious salts produces changes of colour to blue, green, violet, &c. (Vauquelin.)

### Teroxide of Iridium.—$IrO^3$.

Known only in combination with hydrochloric acid or with potash.

Aqueous terchloride of iridium and potassium exhibits but a slight turbidity when mixed with carbonate of potash or soda, but after digestion for some time, deposits a brownish or greenish yellow, gelatinous hydrate of the teroxide, containing however a considerable quantity of potash. The filtrate holds in solution a small quantity of the teroxide, which gives it a yellow colour. The hydrate, if heated after drying, decomposes with sudden decrepitation and evolution of oxygen gas and aqueous vapour, and is projected out of the retort. While yet moist, it dissolves in hot hydrochloric acid, forming a yellow solution, which, when evaporated to dryness, turns red and leaves terchloride of iridium and potassium, from which alcohol does not extract a trace of free terchloride of iridium.

## Iridium and Carbon.

Carbide of Iridium.—A coherent piece of iridium held in the middle of an alcohol-flame, soon becomes covered with a carbonaceous vegetation, which is soft to the touch, stains the fingers, takes fire when slightly heated, afterwards continues to glow, and leaves 80·2 per cent. of iridium.—The iridium on which this carbonaceous mass has been deposited, appears dark-grey, and is completely penetrated by the carbon.—Any oxide of iridium heated in carburetted hydrogen gas or in vapour of alcohol, ether, or any volatile oil, is reduced with incandescence, to carbide of iridium. (Berzelius.)

| | | | Berzelius. |
|---|---|---|---|
| Ir ..... | 99 ..... | 80·49 ..... | 80·2 |
| 4C ..... | 24 ..... | 19·51 ..... | 19·8 |
| $IrC^4$ ..... | 123 ..... | 100·00 ..... | 100·0 |

## Iridium and Phosphorus.

Phosphide of Iridium.—Iridium ignited in phosphorus-vapour takes up a small quantity of phosphorus, and is converted into a mass, which has the appearance of iridium, and, when heated in the air, is converted,

by slow combustion, into a mixture of metallic iridium and phosphate of iridious oxide. (Berzelius.)

## Iridium and Sulphur.

A. Protosulphide of Iridium.—1. Iridium ignited in sulphur vapour, takes up sulphur with slight incandescence, part of the metal, however, remaining uncombined. (Berzelius.)—2. The protosulphide is also formed when one of the higher sulphides is heated out of contact of air. (Böttger, *J. pr. Chem.* 3, 277.)—3. By precipitating an iridious salt with sulphuretted hydrogen, and washing the precipitate with water containing sal-ammoniac or an acid, because pure water dissolves it slightly. (Berzelius.) The sulphide prepared by (2) is grey, like galena, or blackish blue (Böttger); that prepared by (3) is dark yellowish brown. (Berzelius.) Not decomposed by strong ignition in a closed vessel; but when roasted, it gives off sulphurous acid, and is converted into a dark-brown basic sulphate. (Berzelius.) The preparation (3) dissolves in nitric acid, even when cold, with formation of sulphate of the protoxide or sesquioxide of iridium, of a dark green or brown colour, if the acid be cold and in insufficient quantity, or of orange-yellow sulphate of the bioxide, if the acid is in excess, and more especially if it be hot. Any sulphide of platinum that may be present remains for the most undissolved by the cold acid.—(2) is insoluble in nitric acid, and dissolves but sparingly in aqua-regia. (Berzelius; not at all, according to Böttger.)—(3) dissolves in sulphide of potassium more readily than sulphide of platinum; and when precipitated from the solution by acids, it is slightly soluble in pure water, and yields a red-brown solution. Hence the water used to wash the precipitate becomes coloured, but deposits the greater part of the sulphide of iridium when evaporated, in consequence of the concentration of the acid which it contains; if, however, nitric acid has been used for the precipitation, no sulphide of iridium separates out on evaporation, because the nitric acid converts it into sulphate. (Berzelius.)

| | | | Böttger. |
|---|---|---|---|
| Ir | 99 | 86·09 | 85·33 |
| S | 16 | 13·91 | 14·67 |
| IrS | 115 | 100·00 | 100·00 |

B. Sesquisulphide of Iridium.—Formed by precipitating a salt of the sesquioxide with sulphuretted hydrogen. The brown-black precipitate does not become acid by drying; but if subsequently heated, it first gives off water and sulphurous acid—proving that a certain degree of oxidation has taken place—and afterwards sulphur, till the residue is reduced to the protosulphide. With nitric acid and sulphide of potassium it behaves like A (3). Dissolves sparingly in water, forming a yellow solution. (Berzelius.)

| | | |
|---|---|---|
| 2Ir | 198 | 80·49 |
| 3S | 48 | 19·51 |
| $Ir^2S^3$ | 246 | 100·00 |

C. Bisulphide of Iridium.—1. Formed by igniting iridium sal-ammoniac with an equal weight of sulphur. (Vauquelin.)—2. By igniting pulverulent iridium with a mixture of sulphur and carbonate of potash or soda, and exhausting the product with water. (Fellenberg, *Pogg.* 59, 66.)—

3. By precipitating aqueous bichloride of iridium or its compound with chloride of potassium, by hydrosulphuric acid. (Berzelius.) The precipitate is quickly washed with boiling water, then dried in vacuo, and heated in an atmosphere of carbonic acid. (Fellenberg.)—4. With bisulphide of carbon, just as in the preparation (3) of bisulphide of platinum. (Böttger.) If the alcoholic solution of bichloride of iridium deposits a red powder of bichloride of iridium and potassium not previously separated from it, the liquid must be filtered before adding the sulphide of carbon. In the course of four days, the mixture solidifies in a compact black jelly, which, as in the case of platinum, must be well washed with alcohol and water; whereupon, however, a small portion dissolves. (Böttger.) By (1): black coherent powder (Vauquelin); by (3): dark yellowish brown powder (Berzelius); by (4): black, with a few shining points; sandy to the touch, and gritty between the teeth. (Böttger.)

The bisulphide obtained by (1) leaves metallic iridium when ignited in the air. (Vauquelin.) That obtained by (3) behaves like B, when dried in the air and subsequently ignited, and likewise with nitric acid, water, and sulphide of potassium.—(4) leaves metallic iridium when intensely ignited in the air; it does not become acid on exposure to the air; dissolves completely in aqua-regia, but is not decomposed by boiling ammonia, potash, or carbonate of soda. (Böttger.) The product obtained by (2) or (3) is not decomposed by chlorine gas at ordinary temperatures, but when heated to a temperature at which glass softens, it is completely decomposed, yielding chloride of sulphur and chloride of iridium. A small portion of the chloride of iridium sublimes, the quantity being greater the longer the chlorine gas is passed over the sulphide; but the greater part remains at the point where the decomposition takes place. The quantity of chloride of iridium obtained from a given quantity of sulphide varies so much, that in one experiment 81·06, and in another 73·78 per cent. of metal was obtained from it. According to the former result, a chloride of iridium may be supposed to exist, containing more than 1 At. iridium to 1 At. chlorine. (Fellenberg.) [Perhaps a portion of the protochloride of iridium produced was decomposed by the application of too strong a heat, and metallic iridium thereby set free.]

| | | | Vauquelin. (1) | Fellenberg. (2) | Fellenberg. (3) | Böttger. (4) |
|---|---|---|---|---|---|---|
| Ir | 99 | 75·57 | 75 | 75 | 75·92 | 74·81 |
| 2S | 32 | 24·43 | 25 | 25 | 24·08 | 25·19 |
| $IrS^2$ | 131 | 100·00 | 100 | 100 | 100·00 | 100·00 |

D. Tersulphide of Iridium.—Formed by precipitating aqueous terchloride of iridium and potassium with hydrosulphuric acid, the mixture being left for a time in a closed vessel at 60°. Dark yellowish brown precipitate, which behaves like B, when dried in the air and subsequently ignited, or when treated with nitric acid, water, or sulphide of potassium. (Berzelius.)

| | | |
|---|---|---|
| Ir | 99 | 67·35 |
| 3S | 48 | 32·65 |
| $IrS^3$ | 147 | 100·00 |

E. Sulphate of Iridious Oxide.—The solution, when evaporated, deposits a shining, brownish green, amorphous mass, which forms a dark yellowish green solution in water. (Berzelius.)

F. Sulphate of Sesquioxide of Iridium.—When bisulphide or tersulphide of iridium recently precipitated by sulphuretted hydrogen is digested in a quantity of cold nitric acid not sufficient to dissolve it completely, a greenish or reddish brown solution is obtained. (Berzelius.)

G. Sulphate of Iridic Oxide.—The solution of bisulphide or tersulphide of iridium in excess of warm nitric acid is brownish yellow, and yields, on evaporation, a thick yellow syrup. If strong nitric acid be used, the resulting sulphate of iridic oxide remains for the most part undissolved, in the form of a brown amorphous mass, which, after the nitric acid has been poured off, dissolves in water, forming a brownish yellow solution. The aqueous solution is not precipitated by alkalis. The compound is likewise easily soluble in alcohol. (Berzelius.) The dried salt, when strongly heated, gives off sulphuric acid, and leaves a brown *basic* salt, similar to that obtained by roasting sulphide of iridium. (Berzelius.)

## Iridium and Iodine.

Biniodide of Iridium.—Aqueous bichloride of iridium boiled with iodide of potassium and hydrochloric acid, yields the compound $IrI^2$ in the form of a black powder, which gives off its iodine at a temperature near the boiling point of mercury; it is insoluble in water and in acids. (Lassaigne, *J. Chim. méd.* 11, 62.)

## Iridium and Chlorine.

A. Protochloride of Iridium.—*a. Insoluble.*—This compound is formed when iridium, in the finely-divided state in which it is obtained by reducing chloriridiate of potassium with hydrogen gas, is exposed to a stream of chlorine gas at an incipient red heat. The iridium then swells up and forms a light powder, having a dark olive-green colour, and soiling strongly any surface on which it is rubbed. This powder, when very strongly ignited in a porcelain retort, gives off chlorine gas, yields a small sublimate of sesquichloride and bichloride of iridium, and leaves a residue of the metal. Any chloride of osmium that may be mixed with it likewise sublimes, for the most part, under these circumstances. The protochloride thus obtained is insoluble in water, dissolves very sparingly in boiling hydrochloric acid, forming a greenish liquid, and is likewise scarcely soluble in aqua-regia. (Berzelius.) Protochloride of iridium obtained by igniting the bisulphide in chlorine gas, is crystalline, olive-green, and somewhat shining. When treated with water, it gives up a small quantity of a soluble chloride, which colours the liquid yellow. The compound freed from this soluble chloride is slowly reduced, with formation of hydrochloric acid, by ignition in hydrogen gas; when ignited with carbonate of potash, it is decomposed, with separation of a dark grey oxide. But it remains undecomposed when immersed in aqueous hydrosulphate of ammonia, also when boiled with hydrochloric acid, nitric acid, aqua-regia, oil of vitriol, potash, or carbonate of potash. (Fellenberg, *Pogg.* 50, 66.)

*b. Soluble.* Formed by decomposing *a* with solution of potash, treating the separated protoxide with hydrochloric acid, in an excess of which it is partially soluble, and evaporating the brownish green-yellow filtrate, whereupon it turns yellow, and leaves the protochloride of iridium on the

glass in the form of a transparent yellow mass, which, if it has not been too strongly heated, dissolves completely in a small quantity of boiling water, forming a yellow solution; but on adding a larger quantity of water, the greater part of the chloride of iridium is thrown down in the form of a greenish brown precipitate, the liquid remaining yellowish green. —*b* probably contains a small quantity of hydrochloric acid chemically combined. (Berzelius.)

| | | | | Fellenberg. |
|---|---|---|---|---|
| Ir | 99·0 | 73·66 | 73·78 |
| Cl | 35·4 | 26·34 | 26·22 |
| IrCl | 134·4 | 100·00 | 100·00 |

¶ According to Claus (*Ann. Pharm.* 59, 255), the formation of the protochloride of iridium and of its double salts is a problem not yet solved. All the preparations described by Berzelius and others as protochloride of iridium, Claus regards either as sesquichloride, or as mixtures of that compound with metallic iridium. He finds that the bichloride is reduced by sulphurous acid, sulphuretted hydrogen, protochloride of tin, ferrocyanide of potassium, alcohol, and other reducing agents, to the state of sesquichloride; but there the reduction generally stops, excepting that in some cases metallic iridium is separated without the intermediate formation of protochloride. The greyish compound which Berzelius obtained by treating pulverulent iridium with chlorine gas, is likewise, according to Claus, a mixture of sesquichloride and metallic iridium; for, when very finely pounded, and again exposed to the action of chlorine, it absorbs that gas without change of colour, and is thereby brought nearer to the composition of the pure sesquichloride. Moreover, if it be mixed with common salt, and treated with chlorine at nearly the same temperature as before, it yields a product, which, when digested in water, leaves metallic iridium. ¶

B. Sesquichloride of Iridium.—1. Sublimes when iridium, either pure or mixed with nitre, is ignited in chlorine gas, or when protochloride of iridium is ignited *per se*.—2. Formed likewise by igniting iridium with nitre, extracting the potash (together with a small quantity of iridium) from the mass by excess of hot nitric acid, washing the residue with water and dissolving it in hydrochloric acid, whereby chlorine is evolved, and no bichloride formed. The dark yellowish brown solution yields, on evaporation, a syrup, and afterwards a black, amorphous mass. The sesquichloride obtained by (1) is brownish yellow and amorphous, and does not dissolve in water. That obtained by (2) is black, becomes moist in the air, if it has not been too strongly heated, and forms with water a solution which is red-brown, deep yellowish red, brownish yellow, or yellow, according to the degree of concentration. The admixture of a small quantity of the protochloride gives it a green colour; a larger quantity colours it blue or purple. After being heated to the point at which it gives off hydrochloric acid, it dissolves but partially in water, with separation of a brown, flocculent, basic salt. (Berzelius.)

| | | |
|---|---|---|
| 2Ir | 198·0 | 65·09 |
| 3Cl | 106·2 | 34·91 |
| $Ir^2Cl^3$ | 304·2 | 100·00 |

According to Claus, the sesquichloride is the most stable of all the compounds of iridium.

C. Bichloride of Iridium; Iridic Chloride; or Chloriridic Acid.—1. Formed by passing chlorine gas through water in which iridium sal-ammoniac is diffused. (Vauquelin.) In this operation it is necessary to guard against the formation of chloride of nitrogen. (Berzelius.)—2. By digesting an aqueous solution of the sesquichloride with aqua-regia at a gentle heat. (Berzelius.)—3. By dissolving in very strong aqua-regia the residue left by nitric acid in the analysis of osmide of iridium (p. 263; end of 27, β). (Berzelius.) When one of these solutions is evaporated to perfect dryness at a temperature of at least 40°, the water and excess of acid evaporate; a small quantity of sesquichloride of iridium is formed; and the bichloride is left in the form of a black mass, translucent at the edges with a dark red colour, and reduced by cracks to a coarse powder. (Berzelius.) Thomson (*Schw.* 47, 59) obtained it in brown-black, shining tetrahedrons, which had a very rough and bitter taste, gave off 2·625 per cent. of water at a red heat, and when very strongly ignited, left nothing but 44 per cent. of iridium. It sustains a tolerably strong heat without decomposition, and when somewhat strongly heated in a retort, first gives off hydrochloric acid (inasmuch as it obstinately retains a small quantity of water)—whereby iridic oxide is set free, and the compound loses its solubility in water—and afterwards chlorine, in consequence of which a lower chloride is first left behind, and then metallic iridium. (Berzelius.)

| | | | |
|---|---|---|---|
| Ir | 99·0 | | 58·30 |
| 2Cl | 70·8 | | 40·70 |
| $IrCl^2$ | 169·8 | | 100·00 |

Aqueous Bichloride of Iridium, or Hydrochlorate of Iridic Oxide.—The anhydrous compound deliquesces in the air, and dissolves easily in water. A solution containing free acid may be obtained by either of the three methods above described. The concentrated solution is oily, almost black, and appears yellowish red at the edges by transmitted light; as the liquid is further diluted, it becomes brown-red, reddish yellow, and finally, with a very large quantity of water, yellow. At a boiling heat, it gives off chlorine, and is reduced to the state of sesquichloride. The alcoholic solution, when evaporated, gives off an ethereal odour, and deposits scarcely anything but sesquichloride. (Berzelius.)—The solution, when diluted till it becomes yellow, is decolorized by hydrosulphuric acid, ammonia, potash, soda, baryta, lime, zinc-sulphate, ferrous sulphate, ferrocyanide of potassium, and gallic acid; also in 24 hours, by zinc and iron; protochloride of tin decolorizes it, with formation of a few yellow flakes; and mercurous nitrate, with copious formation of orange-yellow flakes. The following substances exert no decolorizing action: sulphuric, hydrochloric, nitric, oxalic, tartaric, citric, and acetic acid, hydrochlorate of manganous oxide, sulphate of ferric oxide, and sulphate of cupric oxide. (Thomson.)—¶ When a tolerably strong solution of the bichloride is mixed with caustic potash, a cherry-red precipitate is first formed, consisting of very small crystals of chloriridiate of potassium, which, however, soon redissolves, the liquid acquiring an olive-green colour. If strong alcohol be then added, a white precipitate with a greenish tinge separates out, consisting of sesquichloride of iridium and potassium; it dissolves readily in water. It appears then that the potash abstracts chlorine from the bichloride, without replacing it by oxygen, acting, in fact, as it would with free chlorine, and producing chloride of potassium and chlorate of potash. The sesquichlorine salt

thus formed is not decomposed by the free potash at ordinary temperatures; but on the application of heat, the colour changes from olive-green to pale yellow. At this point, the sesquichloride of iridium is decomposed, and sesquioxide separated; the latter, however, remains dissolved in the potash, so that no precipitate is formed. But, if the liquid be heated for some time, it absorbs oxygen, and the hydrated sesquioxide is converted into bioxide, and separates in the form of a blue precipitate. (Claus.) ¶

Bichloride of iridium combines with basic metallic chlorides, and dissolves readily in alcohol. (Berzelius.)

D. Iridic Oxychloride.—On mixing the aqueous solution of chloriridiate of potassium with mercurous nitrate, this compound is precipitated in yellowish brown flakes, while corrosive sublimate remains in the liquid. When a larger proportion of mercurous nitrate is added, a light yellow mixture of that substance with calomel is precipitated, and this, when digested in the liquid, is converted into protochloride of iridium, the precipitate at the same time acquiring a green colour. (Berzelius.)

E. Terchloride of Iridium.—Known only in combination with chloride of potassium.

| | | | |
|---|---|---|---|
| Ir | 99·0 | ..... | 48·24 |
| 3Cl | 106·2 | ..... | 51·76 |
| $IrCl^3$ | 205·2 | ..... | 100·00 |

¶ According to Claus, this so-called terchloride of iridium, as well as the corresponding oxide $IrO^3$ is in reality a ruthenium compound, having been formed by Berzelius from iridium containing ruthenium (see p. 388). ¶

## Iridium and Nitrogen.

A. Nitrate of Iridious Oxide, or Iridious Nitrate.—Hydrated protoxide of iridium forms with nitric acid a dingy green solution, which gradually acquires a purple colour; but on evaporating to dryness, and redissolving in water, a greenish yellow liquid is again obtained. (Berzelius.)

B. Ammonio-sesquioxide of Iridium.—Ammonia added to aqueous sesquichloride of iridium, throws down a brown hydrate, which contains iridium, and is consequently reduced with slight detonation when heated. (Berzelius.)

C. *Ammonio-protochloride of Iridium?*—From solutions of protochloride of iridium combined with sal-ammoniac or chloride of potassium, ammonia throws down a light greenish-grey powder. This substance, when heated, undergoes partial fusion; intumesces; gives off, first ammonia, and afterwards hydrochloric acid and sal-ammoniac; and leaves 56·5 per cent. of iridium;—it therefore probably consists of the ammonio-protochloride. (Berzelius.)—Ammonia poured upon pulverized chloriridiate of potassium likewise causes an effervescence arising from evolution of nitric acid, and forms a brown liquid and greyish white precipitate. When the brown liquid is evaporated and the residue dissolved in a very small quantity of water, a small quantity of greyish

white powder is left, and a yellowish brown solution obtained, from which alcohol throws down the yellowish brown protochloride of iridium and ammonium. The greyish white precipitate becomes light greenish grey when dry, and exhibits the above-mentioned relations of ammonio-protochloride of iridium. (Berzelius.)

| | | | | Berzelius. |
|---|---|---|---|---|
| $NH^3$ | 17·0 | ..... | 11·23 | |
| Ir | 99·0 | ..... | 65·39 | ..... 65·5 |
| Cl | 35·4 | ..... | 23·38 | |
| $NH^3$,IrCl | 151·4 | ..... | 100·00 | |

D. Protochloride of Iridium and Ammonium.—$NH^4Cl$, IrCl.—Aqueous sesquichloride of iridium gently heated with sal-ammoniac, is resolved into a precipitate of bichloride of iridium and ammonium, and a green solution of protochloride of iridium and ammonium; and on evaporating the latter, there remains a crystalline mass soluble in hydrated alcohol. — [According to Claus, this compound is identical with the following (see p. 379)].

E. Sesquichloride of Iridium and Ammonium.—When sesquichloride of iridium dissolved in a small quantity of water, is mixed with a quantity of sal-ammoniac not sufficient to convert it completely into the chlorine-salt, and the solution left to evaporate spontaneously, there remains a brown-black, amorphous mass, which remains dry in the air, is insoluble in alcohol, and is partially precipitated in the form of a brown powder on the addition of alcohol to its aqueous solution.—If the sal-ammoniac is in excess, and especially if heat be applied, the liquid acquires a dingy green colour, and deposits bichloride of iridium and ammonium, while protochloride of iridium and ammonium remains in solution. (Berzelius.)

F. Bichloride of Iridium and Ammonium, or Chloriridiate of Ammonium.—*Iridium Sal-ammoniac.*—Precipitated in the form of a dark, cherry-red powder on adding sal-ammoniac to the concentrated aqueous solution of the sesquichloride or bichloride of iridium, or of chloriridiate of sodium.—*Preparation* (p. 259, No. 24).—Small reddish black octohedrons, yielding a dark red powder, and isomorphous with platinum sal-ammoniac.—This compound, when heated to redness, yields 45 per cent. of grey, spongy iridium. (Vauquelin.) When suspended in water through which a stream of chlorine gas is made to pass, it is decomposed, with evolution of nitrogen gas and formation of hydrochloric acid, and converted into hydrochlorate of iridic oxide, with excess of acid. (Descotils.)—1 pt. of the salt dissolves in 20 parts of cold water, forming a dark brown red liquid; but it communicates a perceptible yellow colour even to 4000 parts of water. (Vauquelin.) The aqueous solution supersaturated with ammonia forms a pale yellow mixture, which becomes perfectly colourless when exposed to light, but afterwards turns purple, then violet, and finally assumes a beautiful blue colour. (Vauquelin.)

From an aqueous mixture of hydrochlorate of platinic oxide and hydrochlorate of iridic oxide, sal-ammoniac throws down a mixture of chloroplatinate and chloriridiate of ammonium, and even a small quantity of the latter imparts to the former a brick-red colour. (Descotils.) An analysis by Hermann (*Pogg.* 37, 408) of a mixture of this kind, from the Petersburgh platinum works, containing more iridium than platinum, is given in the following table.

| *Iridium Sal-ammoniac.* | *Crystallized.* | | Vauquelin. |
|---|---|---|---|
| $NH^4Cl$ | 53·4 | 23·92 | |
| Ir | 99·0 | 44·36 | 45 |
| 2Cl | 70·8 | 31·72 | |
| $NH^4Cl,IrCl^2$ | 223·2 | 100·00 | |

| *Platinum-iridium Sal-ammoniac.* | | | Hermann. |
|---|---|---|---|
| $4NH^4Cl$ | 213·6 | 23·92 | |
| Pt | 99·0 | 11·09 | 10·59 |
| 3Ir | 297·0 | 33·27 | 31·76 |
| Pd | | | 1·25 |
| 8Cl | 283·2 | 31·72 | |
| | 892·8 | 100·00 | |

## Iridium and Potassium.

A. Protoxide of Iridium with Potash.—When protochloride of iridium is boiled with potash, part of the resulting protoxide remains dissolved in the excess of potash. The filtrate gradually absorbs oxygen, becoming first purple-red and afterwards dark blue. Also, when carbonate of potash is added to aqueous protochloride of iridium and potassium, a small quantity of the hydrated protoxide thereby produced remains dissolved in the excess of alkali, forming a yellowish green solution. (Berzelius.)

When iridium is ignited with hydrate of potash or with nitre, it oxidizes at the expense of the air or the nitric acid, and forms a blue-black powder, which, as it contains excess of potash, partly dissolves in water, and forms a beautiful blue solution; while another portion, probably containing excess of iridic oxide, remains behind, but dissolves in hydrochloric acid, yielding a blue solution.—If the metal has passed to a higher state of oxidation during the ignition, the aqueous solution of the black powder exhibits a purple colour. (Vauquelin.)

Sesquioxide of Iridium with Potash.—1. When potash is added to hydrochlorate of sesquioxide of iridium, the dark brown hydrate thereby precipitated always contains more or less potash (*vid. Hydrated Sesquioxide of Iridium*, p. 372).—2. The compound is best obtained by heating iridium to whiteness in contact with nitre. The fused product dissolves in a small quantity of lukewarm water, forming a yellowish brown solution; but on dilution with water, the solution deposits a larger quantity of oxide, after some time at ordinary temperatures, but immediately on boiling. This solution, when filtered, colours the paper green, and stops it up by the formation of hydrated protoxide.—3. When finely divided iridium is ignited with hydrate of potash, either mixed with nitre or exposed to the air, a dark yellowish brown solution is formed, partly soluble in water.—*a.* The undissolved portion consists of a large quantity of sesquioxide and a small quantity of potash, together with metallic iridium and the protoxide, which remain behind on dissolving the sesquioxide in acids.—*β.* The solution is deep brown-yellow, contains a proportionately larger quantity of potash, and, when exposed even to slight reducing influences, deposited the [hydrated] protoxide, the reduction taking place the more easily as the liquid is more diluted. (Berzelius.)—[According to Claus, however, the characters just described belong properly to ruthenium, the experiments of Berzelius

having been made with a mixture of iridium and ruthenium (*vid. inf.*)].—4. When bioxide of iridium is fused with carbonate of potash at a very strong heat in a platinum or silver crucible, carbonic acid is evolved, and a yellow or brownish yellow compound of sesquioxide of iridium with potash is obtained. If the mass be taken out of the crucible in the dry state, the surface of the crucible appears bright; but if it be dissolved in the crucible in hot water, the platinum or silver becomes covered with a dark greenish brown crust of oxide.—4. Also, when bichloride of iridium and potassium is ignited with carbonate of potash, a mass is obtained, from which water extracts a compound of potash and sesquioxide of iridium, which tinges it yellow. (Berzelius.)

No compound is obtained by gently igniting the sesquioxide with carbonate of potash. (Berzelius.)

¶ C. Teroxide of Iridium with Potash.—*Iridiate of potash.*—When pure iridium is ignited for two hours with a sufficient quantity of nitre in a silver crucible, a blackish green mass is obtained, which partly dissolves in water, yielding a deep indigo-coloured solution (of basic iridiate of potash), and partly remains undissolved, in the form of a blackish blue crystalline powder (acid iridiate of potash). This powder, when washed, is perfectly neutral and tasteless, gives off a very large quantity of chlorine when immersed in hydrochloric acid, and dissolves completely in that acid, forming an indigo-coloured solution. The powder consists of 61·79 per cent. of iridium, 14·99 oxygen, 11·89 potash and 11·33 water. The quantity of potash, however, is variable, but the iridium and oxygen constantly maintain the proportion of 1 At. iridium to 3 At. oxygen. (Claus, *Ann. Pharm.* 59, 249.) ¶

D. Sulphide of Iridium and Potassium.—When iridium-powder is kept for some time in a state of red-hot fusion with potash and sulphur, and the fused mass when cold digested in water, protosulphide of iridium and potassium is separated (bisulphide, according to Fellenberg), and a green solution formed, from which acids throw down sulphide of iridium. (Berzelius.)

¶ E. Sulphite of Iridious Oxide and Potash.—This salt is obtained in the form of a white powder when the solution from which the salt G has crystallized out is evaporated to a small bulk; it must be washed with water till the wash-water gives with chloride of barium a precipitate perfectly soluble in hydrochloric acid. White powder, having a somewhat crystalline character, nearly tasteless and insoluble in water. Hydrochloric acid dissolves it readily, with evolution of sulphurous acid, and converts it into a yellow prismatic salt, in which 3 At. sulphurous acid are replaced by 3 At. chlorine. It dissolves in caustic potash more easily than in water; and the solution, when heated, is decomposed, after a while, with separation of blue hydrate of iridic oxide. The crystalline salt contains 3 At. water which are given off at 180°; at a higher temperature, complete decomposition takes place, sulphurous acid and sulphur being evolved, and a residue left consisting of iridium and sulphate of potash.

| | *Anhydrous.* | | | Claus. | |
|---|---|---|---|---|---|
| 3KO | 141·6 | 34·64 | 34·29 | 34·48 |
| Ir | 99·0 | 24·15 | 24·74 | 24·33 |
| O | 8·0 | 1·95 | 0·27 | 0·72 |
| $5SO^2$ | 160·0 | 39·26 | 40·70 | 40·47 |
| $3(KO,SO^2) + IrO,2SO^2$ | 408·6 | 100·00 | 100·00 | 100·00 |

| | *Crystallized.* | | | Claus. |
|---|---|---|---|---|
| 3KO | 141·6 | .... | 31·22 | |
| Ir | 99·0 | .... | 21·82 | |
| O | 8·0 | .... | 1·76 | |
| $5SO^2$ | 160·0 | .... | 35·27 | |
| 5HO | 45·0 | .... | 9·93 | ..... 10·00 |
| $3(KO,SO^2)+IrO,2SO^2+5Aq$ | 453·6 | .... | 100·00 | |

(Claus, *Ann. Pharm.* 63, 352.) ¶

F. Protochloride of Iridium and Potassium. — KCl,IrCl. — 1. Formed by mixing the solution of protochloride of iridium in hydrochloric acid with chloride of potassium, and evaporating to dryness.— 2. By adding chloride of potassium to an alcoholic solution of sesquichloride of iridium, and distilling off the alcohol. A small quantity of metallic iridium then separates, and part of the protochloride of iridium and potassium is precipitated, while the rest remains in solution, colouring the liquid greenish brown ; and on evaporating this solution, indistinct crystals are obtained, which are dark green while moist and become yellowish green when dry. The salt is insoluble in alcohol, which however does not precipitate it completely from its aqueous solution. (Berzelius.)—[According to Claus, this is really a sesqui-chlorine compound (see page 379). No analysis of it is given by Berzelius.]

G. Sesquichloride of Iridium and Potassium.—¶ *a. With 3 At. Chloride of Potassium.*—When finely pulverized bichloride of iridium and potassium is immersed in 8 times its weight of water, and sulphurous acid gas passed through the liquid till the whole of the salt is dissolved, the bichloride of iridium is reduced to sesquichloride, with formation of sulphuric and hydrochloric acids ; any platinum, palladium, osmium, rhodium, or ruthenium that may be mixed with the iridium-salt remain undissolved. On adding a highly concentrated solution of carbonate of potash in quantity sufficient to saturate the free acids, a light olive green precipitate is formed, consisting of small prisms having a diamond lustre, and composed of $3KCl,Ir^2Cl^3+3$ Aq. — 2. The same compound may be obtained by gently igniting the bichloride of iridium and potassium, either alone, or mixed with one-third of its weight of carbonate of potash, exhausting with water, and leaving the solution to crystallize. This mode of preparation, however, is less advantageous than the former, because a large proportion of the salt which it should yield is entirely decomposed during the process, and metallic iridium separated.—The crystallized salt effloreses rapidly in dry air; it is insoluble in alcohol, but easily soluble in water ; alkalis decompose it with difficulty. Nitrate of silver throws down a precipitate in which the 3 At. potassium are replaced by silver.

| | *Dried in the air.* | | | Claus (*mean*). | | Or : | | | |
|---|---|---|---|---|---|---|---|---|---|
| 3K | 141·6 | .... | 22·30 | .... | 22·48 | 3KCl | 247·8 | .... | 42·47 |
| 2Ir | 198·0 | .... | 37·35 | .... | 37·25 | $Ir^2Cl^3$ | 304·2 | .... | 57·53 |
| 6Cl | 212·4 | .... | 40·35 | .... | 40·25 | | | | |
| $3KCl+Ir^2Cl^3$ | 552·0 | .... | 100·00 | .... | 99·98 | | 552·0 | .... | 100·00 |

| | *Crystallized.* | | | Claus. |
|---|---|---|---|---|
| 3KCl | 247·8 | .... | 40·90 | |
| $Ir^2Cl^3$ | 304·2 | .... | 50·19 | |
| 6HO | 54·0 | .... | 8·91 | ..... 9·45 |
| $3KCl,Ir^2Cl^3+6Aq.$ | 606·0 | .... | 100·00 | |

The solution from which the greater part of this salt has been precipitated by carbonate of potash, retains its olive-green colour at ordinary temperatures, but if heated for a while, it turns red and afterwards light-yellow. Several compounds are then formed, which separate on evaporation, or on mixing the concentrated solution with water, and are difficult to obtain in a state of purity. They all contain sulphurous acid, chlorine, and protoxide of iridium; they are sparingly in water; give off sulphurous acid when heated; dissolve with tolerable facility in hydrochloric acid, with evolution of sulphurous acid, and are thereby converted into easily soluble crystalline salts. These compounds will be specially described further on. (Claus, *Ann. Pharm.* 63, 341.) ¶

*b. With 2 At. Chloride of Potassium.*—1. Formed by mixing the aqueous solution of sesquichloride of iridium with a quantity of chloride of potassium not sufficient to convert it completely into the double chloride, and leaving it to evaporate at ordinary temperatures or at a very gentle heat. If the chloride of potassium be added in excess, and the solution warmed, it becomes dingy green, and deposits bichloride of iridium and potassium, while the protochloride of iridium and potassium remains in solution.—2. By heating a mixture of bichloride of iridium and potassium, and finely divided iridium to redness in a glass tube, exhausting the unfused mass with water, evaporating the solution—whereupon a small quantity of bichloride of iridium and potassium separates out—and evaporating the decanted liquid to a smaller bulk.—Brown-black (inclining to green, if mixed with protochloride of iridium and potassium); amorphous, permanent in the air, easily soluble with dark brown colour in water, but insoluble in alcohol, which partly precipitates it from its concentrated aqueous solution, in the form of a brown powder; hence the salt may be purified by precipitation with alcohol. (Berzelius.)—On evaporating the aqueous solution to dryness, there is sometimes obtained a mixture of bichloride of iridium and potassium, and a dark blue or dark green chlorine-salt, which, being more easily soluble, may be dissolved out by a small quantity of water, and from which potash precipitates the blue oxide. If chloride of potassium has been previously added, the liquid which stands above the bichloride of iridium and potassium is blue or violet (green, if it contains iron); but it soon deposits protochloride of iridium and potassium, while the sesqui-chlorine compound remains dissolved, forming a yellowish brown solution. (Berzelius.)

| | *Dried at* 100°. | | | Berzelius. |
|---|---|---|---|---|
| 2KCl | 149·2 | 32·91 | | 32·00 |
| 2Ir | 198·0 | 43·67 | | 43·91 |
| 3Cl | 106·2 | 23·42 | | 24·09 |
| $2KCl,Ir^2Cl^3$ | 453·4 | 100·00 | | 100·00 |

H. Bichloride of Iridium and Potassium.—*Chloriridiate of Potassium.*—1. Formed by passing chlorine gas over a gently ignited and intimate mixture of finely divided iridium and chloride of potassium; filtering the solution to separate the unaltered iridium; dissolving the unfused, black-brown mass in hot water; mixing it with aqua-regia (to furnish additional chlorine to any sesquichloride of iridium that may be present); evaporating to dryness; extracting the excess of chloride of potassium by small quantities of cold water; dissolving the residue in boiling water; adding a small quantity of aqua-regia to the solution; and evaporating to the crystalline point. The blackish-brown mass may also be first treated with cold water to extract the free chloride of potassium

and afterwards with boiling water to dissolve the double chloride. (Berzelius.)—2. By adding chloride of potassium to an aqueous solution of bichloride of iridium. (Vauquelin.)—This compound is likewise obtained in the course of the analysis of platinum ore (p. 262, No. 27).—Small, shining, reddish black, regular octohedrons, which yield a dark red powder. (Vauquelin.)—Decrepitates when heated. (Vauquelin.)—Not decomposed by gentle ignition; but when strongly heated, it is converted into sesquichloride of iridium and potassium (Berzelius), and when still more strongly ignited, leaves a residue of iridium mixed with chloride of potassium. (Vauquelin.) If the compound be intensely ignited till the chloride of potassium evaporates, the iridium remains in the form of a skeleton, consisting of metallic-looking scales. (Wöhler, *Pogg.* 31, 167.) When ignited in an atmosphere of hydrogen, it gives off 29 per cent. of chlorine, and is converted into a mixture of iridium and chloride of potassium. (Berzelius.) With excess of aqueous potash it behaves in the same manner as iridium sal-ammoniac with excess of ammonia. (Vauquelin.)—Dissolves slowly in cold water, and in 15 pts. of boiling water, from which only $\frac{1}{3}$ of the original quantity separates out on cooling. (Vauquelin, *Ann. Chim.* 88, 234; 90, 260.) In the state of powder, it dissolves quickly in pure boiling water, forming a liquid, which appears deep red in the mass, but yellow in thin films. Does not dissolve in water saturated with chloride of calcium and other salts, or in alcohol, and is completely precipitated from its aqueous solution by alcohol, in the form of a dark red powder, especially if the alcohol contains chloride of potassium in solution. (Berzelius.)

| | | | | Vauquelin. |
|---|---|---|---|---|
| KCl | 74·6 | .... | 30·52 | |
| Ir | 99·0 | .... | 40·51 | ..... 37 |
| 2Cl | 70·8 | .... | 28·97 | |
| $KCl,IrCl^2$ | 244·4 | .... | 100·00 | |

This iridium-salt crystallizes in various proportions with the corresponding platinum-salt, with which it is isomorphous. A compound of this nature, examined by Hermann (*Pogg.* 37, 408) contained 8 per cent. (1 At.) of iridium and 32 per cent. (4 At.) of platinum.

I. Terchloride of Iridium and Potassium.—When osmide of iridium ignited with nitre and purified as completely as possible (p. 262, No. 23), is distilled with aqua-regia, the residue dissolved in water in the retort, and the filtrate evaporated to dryness, and afterwards exhausted with successive small quantities of water, the first solution appears slightly coloured and contains scarcely anything but chloride of potassium; the following solutions have a dark rose-colour, proceeding from terchloride of iridium and potassium; and the last are coloured yellow by bichloride of iridium and potassium, the quantity of which is greater than that of either of the other salts. The red solutions are evaporated by themselves; the residue pulverized and freed from excess of chloride of potassium by digestion in alcohol of specific gravity 0·84, which thereby acquires but a very slight red tinge; the residual brown powder dissolved in water; and the rose-coloured solution abandoned to spontaneous evaporation, whereupon the compound crystallizes out.—This compound is not obtained by saturating the aqueous solution of bichloride of iridium and potassium with chlorine gas, or by evaporating it with aqua-regia or with chlorate of potash and hydrochloric acid.—Forms rhombic prisms with dihedral summits, which

are even deceptively like those of sesquichloride of rhodium and potassium; they are brown by transmitted, and ruby-red by reflected light. When perfectly dried and then heated in an atmosphere of hydrogen gas, it is resolved into 24·17 per cent. of chlorine, which goes off as hydrochloric acid, 23·92 of iridium, and 51·91 of chloride of potassium. Its rose-coloured aqueous solution when repeatedly evaporated, deposits protochloride of iridium in the form of a green powder. Alcohol precipitates the compound from its aqueous solution in the form of a pale rose-coloured powder; a small quantity, however, remains dissolved with a pale red colour, and is left unaltered when the alcohol is distilled off. Sulphuretted hydrogen does not form an immediate precipitate in the aqueous solution, but only when digested with it in a stoppered bottle at the temperature of 60°; and even then the precipitation is imperfect. (Berzelius.)

| | | | Berzelius. |
|---|---|---|---|
| 3KCl | 223·8 | 52·17 | 51·91 |
| Ir | 99·0 | 23·08 | 23·92 |
| 3Cl | 106·2 | 24·75 | 24·17 |
| $3KCl,IrCl^3$ | 429·0 | 100·00 | 100·00 |

¶ According to Claus, the compound obtained by Berzelius is really a ruthenium-compound, having been obtained from osmide of iridium containing ruthenium. On the contrary, the compound formed by fusing pure iridium with nitre, and treating the product with hydrochloric acid, contains, not terchloride but bichloride of iridium. (*Ann. Pharm.* 59, 249.) ¶

¶ K. Sulphite of Iridious Oxide with Chloride of Potassium.—Formed by treating the salt G (p. 385) with hydrochloric acid. A light yellow solution is then obtained, which, on evaporation, yields pale yellow prisms, very soluble in water, and having an astringent and somewhat sweetish taste. At a red heat, the salt is resolved into sulphurous acid, iridium, and a mixture of chloride of potassium and sulphate of potash. (Claus, *Ann. Pharm.* 63, 354.)

| | | | Claus. |
|---|---|---|---|
| 3K | 117·6 | 29·79 | |
| I | 99·0 | 25·02 | 25·00 |
| O | 8·0 | 2·02 | |
| $2SO^2$ | 64·0 | 16·26 | 17·33 |
| 3Cl | 106·2 | 26·91 | 26·47 |
| $3KCl + IrO,2SO^2$ | 394·8 | 100·00 | |

L. Chlorohyposulphate of Iridious Oxide with Sulphate of Potash.—When the mother-liquor from which the following red salt M has separated, is evaporated to a small bulk, a mixture of the white salt E, with a further portion of the salt M, separates from it in the form of powder; and on decanting the remaining liquid, concentrating it still further, and mixing it with a large quantity of water, a flocky, whitish yellow precipitate separates out, which, if heated together with the liquid, collects at the bottom of the vessel in the form of a dirty yellow, viscid mass, consisting of the salt L mixed with the white salt E. The liquid is then boiled till the whole is dissolved, the solution filtered hot, and then left to itself for several days, whereupon the salt L separates out in a state of purity, and forming a translucent mass having a fine amber colour and the consistence of turpentine. It dries up to an amorphous, brittle, translucent substance, which yields a lemon-yellow powder.—The salt is decomposed by water, part of it dissolving, and the rest being

converted into the white salt E; hence its preparation presents great difficulty. (Claus, *Ann. Pharm.* 63, 351.)

| | | | | | Claus. |
|---|---|---|---|---|---|
| 4KO | 188·8 | .... | 29·96 | ..... | 29·45 |
| 2Ir | 198·0 | .... | 31·42 | ..... | 31·48 |
| 2O | 16·0 | .... | 2·55 | ..... | 2·55 |
| $6SO^2$ | 192·0 | .... | 30·46 | ..... | 30·82 |
| Cl | 35·4 | .... | 5·61 | ..... | 5·70 |
| $4(KO,SO^2) + 2IrO,S^2O^4Cl$ | 630·2 | .... | 100·00 | ..... | 100·00 |

The acid supposed to be combined with the protoxide of iridium in this and the two following compounds, is formed from hyposulphuric acid, $S^2O^5$, by the substitution of 1 At. chlorine for 1 At. oxygen.

M. Chloro-hyposulphate of Iridious Oxide with Chloride of Potassium.—$4KCl + 2IrO,S^2O^4Cl$.—Formed by treating the following salt N, with hydrochloric acid, in which it dissolves easily, forming a yellow solution. On evaporating the liquid, sulphurous acid is given off, and when a certain degree of concentration is attained, the solution becomes red, and yields prismatic crystals having an intense red colour and a diamond lustre. The salt has a sweet, astringent taste, dissolves readily, with a yellow colour, in water, but is insoluble in alcohol. The crystals when moistened with water, combine with it, become opaque, assume a yellow colour, and lose their lustre. When they are strongly heated, sulphurous acid escapes, and a residue is left consisting of iridium and chloride of potassium. Alkalis slowly decompose the salt, and aqua-regia converts it, after some time, into a salt of iridic chloride. The crystals when dried in the air, contain 5·6 per cent. of water = 4 At. which is expelled with difficulty at 180°. (Claus, *Ann. Pharm.* 63, 349.)

| | *Anhydrous.* | | | | Claus. | | |
|---|---|---|---|---|---|---|---|
| 4K | 156·8 | .... | 25·65 | ..... | 25·24 | .... | 24·30 |
| 2Ir | 198·0 | .... | 32·23 | ..... | 32·22 | .... | 32·19 |
| 2O | 16·0 | .... | 2·66 | ..... | 3·08 | .... | 4·99 |
| $2SO^2$ | 64·0 | .... | 10·52 | ..... | 10·23 | .... | 10·00 |
| 5Cl | 177·0 | .... | 28·94 | ..... | 29·23 | .... | 28·52 |
| $4KCl + 2IrO,S^2O^4Cl$ | 611·8 | .... | 100·00 | ..... | 100·00 | .... | 100·00 |

| | *Crystallized.* | | | Claus. | |
|---|---|---|---|---|---|
| 4K | 156·8 | .... | 24·20 | | |
| 2Ir | 198·0 | .... | 30·56 | | |
| 2O | 16·0 | .... | 2·47 | | |
| $2SO^2$ | 64·0 | .... | 9·88 | | |
| 5Cl | 177·0 | .... | 27·33 | | |
| 4HO | 36·0 | .... | 5·56 | ..... | 5·6 |
| $4KCl + 2IrO,S^2O^4Cl + 4Aq.$ | 647·8 | .... | 100·00 | | |

N. Chloro-hyposulphate of Iridious Oxide with Sulphite of Potash and Chloride of Potassium.—This compound is obtained by dissolving 1 part of sesquichloride of iridium and potassium (G, *a*, page 385) in 12 parts of water, mixing the liquid with a solution of ½ pt. carbonate of potash previously saturated with sulphurous acid, heating the mixture in a porcelain basin till the olive-green colour changes to red, and setting it aside for a few days. The salt then separates out in small, flesh-coloured or minium-coloured, six-sided prisms, which are partially decomposed by solution in hot water, but dissolve in caustic potash more easily than in water, forming a yellow solution which becomes dark

green when heated, but recovers its yellow colour on being saturated with nitric acid, a white precipitate being at the same time produced. If the alkaline liquid be heated without addition of nitric acid, the blue hydrate of iridic oxide separates out. Aqua-regia slowly converts the salt into a new compound containing bichloride of iridium. The salt after being dried in the air gives off from 14·7 to 15 per cent. of water (= 12 At.) at 180°.

| | | | Claus (*mean*). |
|---|---|---|---|
| 4K | 156·8 | 25·26 | 25·33 |
| 2Ir | 198·0 | 31·79 | 31·59 |
| 4O | 32·0 | 5·14 | 4·86 |
| $4SO^2$ | 128·0 | 20·70 | 20·91 |
| 3Cl | 106·2 | 17·11 | 17·31 |
| $2(KO,SO^2)+2KCl+2IrO,S^2O^4Cl$ | 621·0 | 100·00 | 100·00 |

| *Crystallized.* | | | Claus. |
|---|---|---|---|
| 4K | 156·8 | 21·51 | |
| 2Ir | 198·0 | 27·15 | |
| 4O | 32·0 | 4·37 | |
| $4SO^3$ | 128·0 | 17·51 | |
| 3Cl | 106·2 | 14·56 | |
| 12HO | 108·0 | 14·90 | 14·75—15·00 |
| $2(KO,SO^2)+2KCl+2IrO,S^2O^4Cl+12Aq.$ | 729·0 | 100·00 | |

The composition of this salt may likewise be represented by the formula, $4(KO,SO^2)+Ir^2Cl^3$, according to which it might be regarded as a compound of sesquichloride of iridium with sulphite of potash. It appears however to contain, not the sesquioxide, but the protoxide of iridium, and hence the formula above given is to be preferred. The relation between this salt and the preceding compounds L and M, tends likewise to the same conclusion; for the salt M is evidently formed from N by the substitution of 2 At. KCl for 2 At. $KO,SO^2$ (or of 2Cl for $2SO^3$); and if N be regarded as a compound of $4(KO,SO^2)$ with $Ir^2Cl^3$, it is not very apparent why the hydrochloric should decompose only half the sulphite of potash contained in it. The salt L is evidently formed from N by the substitution of 2 At. sulphite of potash for 2 At. chloride of potassium. (Claus, *Ann. Pharm.* 63, 344–348.) ¶

## Iridium and Sodium.

A. Protochloride of Iridium and Sodium. — NaCl, IrCl. — 1. Formed by mixing a solution of protochloride of iridium in hydrochloric acid with common salt.—2. By adding sal-ammoniac to a hot concentrated solution of sesquichloride of iridium and sodium. By this means, bichloride of iridium and ammonium is precipitated, while protochloride of iridium and sodium remains in solution. The latter is green, and leaves, on evaporation a green, deliquescent, saline mass, soluble in alcohol. (Berzelius.)

B. Sesquichloride of Iridium and Sodium.—*Chloriridiate of Sodium.*—Sesquichloride of iridium dissolved in water, is not decomposed on evaporation, even with excess of common salt, (as it is with chloride of potassium,) but forms with it a coal-black salt, which does not fuse when heated, deliquesces in the air, and dissolves in water and alcohol, forming solutions whose colour resembles that of venous blood diluted with water.

C. Bichloride of Iridium and Sodium.—Obtained by a process similar to the first of those described for the preparation of the corresponding potassium salt, viz., by heating a mixture of iridium and common salt in chlorine gas, &c.—Black tables and four-sided prisms with dihedral summits, isomorphous with the corresponding platinum-salt; when heated, they leave the anhydrous salt in the form of a brownish grey powder. They are easily soluble in water. Sal-ammoniac added to the solution, throws down a precipitate of chloriridiate of ammonium. (Berzelius.)

| | *Anhydrous.* | | | | *Crystallized.* | | |
|---|---|---|---|---|---|---|---|
| NaCl ..... | 58·6 | .... | 25·66 | NaCl ..... | 58·6 | .... | 20·75 |
| Ir ..... | 99·0 | .... | 43·34 | $IrCl^2$ ..... | 169·8 | .... | 60·13 |
| 2Cl..... | 70·8 | .... | 31·00 | 6HO ..... | 54·0 | .... | 19·12 |
| $NaCl,IrCl^2$ | 228·4 | .... | 100·00 | +6Aq. ..... | 282·4 | .... | 100·00 |

## Iridium and Barium.

When sulphate of iridic oxide is precipitated with chloride of barium, the sulphate of baryta carries down with it a large quantity of iridic oxide, in a state of intimate combination, acquiring thereby a rusty yellow colour. (Berzelius.)

## Iridium and Calcium.

Milk of lime added to an acid solution of the blue oxide, throws down a blue compound of the oxide with lime. (Vauquelin.)

## Iridium and Aluminum.

An aqueous mixture of a blue salt of iridium with alum, yields, when treated with ammonia or potash, a blue precipitate, less soluble in excess of alkali than the pure blue oxide. (Vauquelin.)

## Iridium and Chromium.

Chromate of potash added to hydrochlorate of iridic oxide, throws down an olive-green powder.

## Iridium and Arsenic.

Arseniate of potash heated with hydrochlorate of iridic oxide, throws down a brown precipitate. (Thomson.)

## Iridium and Tin.

Alloy of Iridium and Tin.—1 part of iridium unites with 4 parts of tin, at an intense red heat, forming a dull white, easily crystallisable, hard, malleable alloy. (Vauquelin.)

### Iridium and Lead.

Alloy.—1 part of iridium and 8 parts of lead, heated together to an intense red heat, unite and form an alloy which is ductile, but much harder and whiter than lead, and gives up its lead to nitric acid, the iridium remaining in the form of a black powder. (Vauquelin.) When this alloy is cupelled, the iridium is left behind in the form of a soft black powder. (Tennant.)

### Iridium and Copper.

Alloy.—1 part of iridium combines at a white heat with 4 parts of copper, forming a ductile, pale red alloy, which is much harder than copper, and behaves with nitric acid in a similar manner to the lead alloy.

### Iridium and Mercury.

Amalgam of Iridium.—Sodium-amalgam immersed in an aqueous solution of chloriridiate of sodium, yields a viscid amalgam, its formation being attended with separation of greyish black flakes and violent evolution of hydrogen gas. The amalgam, when very strongly ignited, leaves a black powder, from which boiling nitric acid still extracts a small quantity of mercury, leaving a residue of pure iridium, soluble in boiling aqua-regia. (Böttger, *J. pr. Chim.* 12, 252.)

### Iridium and Silver.

A. Alloy.—One part of iridium unites but imperfectly with 2 parts of silver. (Vauquelin.)—Tennant likewise obtained a malleable alloy, which, however, appeared to be only a mixture.

¶ B. Chloride of Iridium and Silver.—$3AgCl + Ir^2Cl^3$.—Nitrate of silver forms with chloriridiate of potassium, a deep indigo-coloured, flocculent precipitate, which, however, becomes paler in a few seconds, and finally loses its colour altogether. The supernatant liquid is colourless, and contains nitrate of potash and free nitric acid, but no iridium. The reaction, which is attended with evolution of oxygen, takes place as follows :

$$3(AgO,NO^5) + 2(KCl,IrCl^2) = 3AgCl,Ir^2Cl^3 + 2(KO,NO^5) + NO^5 + O.$$

A boiling solution of chloriridiate of potassium forms the same compound immediately, without the intermediate production of any blue substance. The compound is insoluble in water and in acids, and sparingly soluble in caustic ammonia. If it be covered with a strong solution of ammonia, and allowed to stand in contact with it for a few days, one portion dissolves, while another portion is converted into a shining, crystalline powder, of a light yellow colour, with greenish iridescence. This crystalline powder, which, when examined by the microscope, appears to be composed of rhombohedrons having a diamond lustre, is merely the same compound in the crystalline state. (Claus, *Ann. Pharm.* 63, 338.)

| | | Claus. | | |
|---|---|---|---|---|
| 3Ag | 324·0 .... 44·15 | 46·36 | 45·01 | 44·00 |
| 2Ir | 198·0 .... 26·89 | 25·82 | 26·96 | 26·90 |
| 6Cl | 212·4 .... 28·96 | 27·82 | 28·03 | 29·10 |
| $3AgCl,Ir^2Cl^3$ | 734·4 .... 100·00 | 100·00 | 100·00 | 100·00 ¶ |

## Iridium and Gold.

Alloy.—Malleable compound, having a colour not differing much from that of gold; when it is treated with aqua-regia, the iridium is left behind in the form of a black powder.

## Iridium and Platinum.

Alloys.—Equal weights of the two metals form a brittle alloy, capable of welding to a certain extent. (Berzelius.) The alloy of 1 pt. iridium and 10 platinum fused together in the flame of the oxy-hydrogen blowpipe, is very malleable, susceptible of hardening, does not tarnish, and when laid upon copper, serves for metallic mirrors. (Gaudin, *J. pr. Chem.* 16, 55.) The alloy of platinum with a few parts per cent. of iridium is ductile, much harder than pure platinum, and more capable of resisting the action of fire and of chemical reagents. (Berzelius.)

*a. Native alloy of Iridium and Platinum*, the so-called *Native Iridium*, from the Ural.—Cubo-octohedrons, whose specific gravity varies from 21·85 to 22·65 and 22·8. (G. Rose, *Pogg.* 34, 377; *comp.* Breithaupt, *Schw.* 69, 96.)

*b.* A mineral from Brazil, said to be an osmide of iridium. White round grains, of specific gravity 16·94. (Svanberg, *Jahresbericht.* 15, 205.)

| | Svanberg. | |
|---|---|---|
| | *a.* | *b.* |
| Pt | 19·64 | 55·44 |
| Pd | 0·89 | 0·49 |
| R | | 6·86 |
| Ir | 76·85 | 27·79 |
| Os | | trace |
| Fe | | 4·14 |
| Cu | 1·78 | 3·30 |
| | 99·16 | 98·02 |

Iridium likewise combines with *Osmium*.

¶ Chapter XLIII.

# RUTHENIUM.

Claus. *Pogg.* 64, 192, and 624; 65, 200; abstr. *Berz. Jahresb.* 25, 205; *Ann. Pharm.* 56, 257.—Further, *Ann. Pharm.* 59, 234.—Further, *Ann. Pharm* 63, 259.

*History.* Osann, in 1828, (*Pogg.* 14, 329,) described his experiments with the residue of Siberian platinum ore, after treatment with aqua-regia, and thought that he had discovered in it two new metals, one of which he called *Pleuranium*, and the other *Ruthenium*. This investigation, which led to no definite results, was afterwards taken up by Claus, who succeeded in denonstrating the existence of one new metal in the platinum residues. To this metal he gave the name of *Ruthenium*, because it occurred in small quantity in the substance which Osann had distinguished by the name of oxide of ruthenium, which, however, Claus found to consist for the most part of silica, titanic acid, ferric oxide, and zirconia. The new metal has since been more particularly examined by Claus, to whom indeed we are indebted for all that is at present known on the subject.

*Sources.* In platinum ore, both Russian and American, but in quantity not exceeding 1 or $1\frac{1}{2}$ per cent. It forms part of the native osmide of iridium, in which it is associated with platinum, rhodium, iridium, and osmium. The different varieties of this mineral analyzed by Claus, contained from 3 to 6 per cent. of ruthenium, 10 platinum, $1\frac{1}{2}$—2 rhodium, together with traces of copper, iron, and palladium. The *Irite* discovered by Hermann likewise contains 3 per cent. of ruthenium, together with rhodium, platinum, iridium, osmium, ferrous oxide, chromic oxide, alumina, silica, and iridic oxide. Ruthenium is not found in the portion of the platinum ore which is soluble in aqua-regia.

*Preparation. a. Claus's original method.* (*Pogg.* 65, 200.)—1. Fifteen pounds of platinum residue were mixed with nitre, (each pound of the former with 2 lbs. of the latter,) the mixture fused for two hours at a strong heat in a hessian crucible, and the fused mass, after cooling, pulverized and exhausted with water. The brown-red solution contained chromate, osmiate, silicate, iridiate, rutheniate, and titanate of potash, (the quantities according to the preceding order,) together with nitrate of potash and free alkali.

2. The greater part of the ruthenium, however, remained in the

residue which was left after treating the fused mass with water. This residue was mixed in a retort with half its weight of aqua-regia and a little water, and the liquid distilled nearly to dryness, whereupon osmic acid passed over into the receiver. The contents of the retort were exhausted with water, and the solution filtered; the insoluble residue (*a*) weighed 11½ lbs.

3. The filtered liquid treated with carbonate of potash yielded a precipitate of ferric and ruthenic oxide, from the solution of which in hydrochloric acid, zinc threw down a small quantity of ruthenium; but the greater part remained in the liquid, together with the oxides of iron and zinc.

4. The brown alkaline solution from which the ferric and ruthenic oxides had been precipitated, became nearly colourless when left to stand in wooden vessels, and, if afterwards mixed with potash-ley, yielded a white precipitate, which turned brown after a while, but became white again when dry. Hydrochloric acid extracted from it a metallic oxide, which gave a green colour to the liquid, while titaniferous silica, together with alumina, remained undissolved. The hydrochloric acid solution assumed an orange-yellow colour when boiled with nitric acid, and blue when treated with sulphuretted hydrogen.

5. The alkaline solution (4) was evaporated in an iron vessel, whereupon a large quantity of blue oxide of iridium separated out. This was dissolved in aqu-regia, the iridium precipitated from the concentrated solution by means of chloride of potassium, the mother-liquor evaporated to dryness, and the residue reduced with hydrogen. The metallic powder thereby produced contained an alloy of iridium and ruthenium, together with a small quantity of rhodium.

6. This metallic powder, together with a portion of the black powder (2, *a*) insoluble in aqua-regia, which still contained considerable quantities of iridium, chrome iron ore, silicates, ruthenium, and rhodium, was then mixed with its own weight of nitre, and fused for two hours at a white heat—the cooled mass exhausted with distilled water—and the orange-yellow solution, mixed with a very small quantity of nitric acid, which threw down a bulky, velvet-black precipitate of impure rutheniate of potash containing silica. The concentrated hydrochloric acid solution of this compound, freed from silica by careful evaporation and re-solution in water, deposited, when mixed with chloride of potassium, a precipitate of sesquichloride of ruthenium and potassium; and, on heating this precipitate in an atmosphere of hydrogen, and dissolving out the chloride of potassium by water, the metallic *Ruthenium* was obtained in the form of a dark grey powder.

*b. Claus's more recent method.* (*Ann. Pharm.* 59, 234.) — Osmide of iridium is pulverized as finely as possible in a cast-iron mortar; the particles of iron which are rubbed off the mortar, dissolved out by hydrochloric acid; and the remaining metallic powder mixed with common salt, and heated to low redness in a current of moist chlorine gas. The disintegrated mass is then digested in cold water, and the concentrated solution, which is brown-red and almost opaque, mixed with a few drops of ammonia, and heated in a porcelain capsule, whereupon it deposits a copious black-brown precipitate, consisting of sesquioxide of ruthenium and osmic oxide. This precipitate, after washing with a sufficient quantity of nitric acid, is heated in a retort, till all the free acid has passed over, and the osmium is expelled in the form of osmic acid. The contents of the retort are then taken out and ignited for an hour in a

silver crucible with caustic potash free from silica, and the ignited mass softened and dissolved by cold distilled water. The solution is left in a corked bottle for two hours to clarify; the perfectly transparent liquid, which has a beautiful orange-yellow colour, separated by a syphon from the undissolved portion; and the alkaline solution neutralized with nitric acid. Velvet-black sesquioxide of ruthenium is then deposited; and this, when washed, dried, and ignited in an atmosphere of hydrogen, yields perfectly pure metallic *Ruthenium*. This mode of separating ruthenium from all the other platinum metals, except osmium, is based upon the property possessed by the sesquichloride of ruthenium, of splitting up, when heated, into free hydrochloric acid and sesquioxide of ruthenium. Osmic oxide mixes with the oxide of ruthenium, because the solution contains bichloride of osmium, which is decomposed in a similar manner. Not more than a third of the osmide of iridium is decomposed by the above-described treatment with chlorine gas; to obtain complete decomposition, therefore, the process must be repeated three or four times.

*Properties.* Ruthenium obtained by the first of the above processes is a dark grey powder; by the second process, it is obtained in small, angular, porous lumps, having a whitish grey colour and metallic lustre, and bearing a strong resemblance to iridium. Very brittle. Specific gravity 8·6 at 16°. This is much less than the density usually attributed to iridium (p. 370); it is probable, however, that the two metals do not really differ much in density; for a specimen of porous iridium prepared from the blue oxide by reduction with hydrogen, had a specific gravity of only 9·3. Ruthenium does not fuse even in the flame of the oxy-hydrogen blowpipe.

## *Compounds of Ruthenium.*

### Ruthenium and Oxygen.

The affinity of ruthenium for oxygen is greater than that of any of the other platinum-metals, except osmium. When heated to redness in the air, it oxidizes readily, and is converted into a bluish black oxide, which does not part with its oxygen at a white heat. The metal is nearly insoluble in acids, even aqua-regia dissolving but a trace. It is not dissolved by fused bisulphate of potash. By fusion with nitre, however, it is converted into a blackish green mass, which, when treated with water, yields an orange-yellow solution of rutheniate of potash; and this when mixed with acids, yields a precipitate of black ruthenic oxide. Caustic potash, at a red heat, dissolves the metal as easily as nitre.

#### A. Protoxide of Ruthenium, or Ruthenious Oxide. RuO.

Formed by strongly heating a mixture of 1 At. bichloride of ruthenium, and rather more than 1 At. carbonate of soda in a stream of carbonic acid gas, and removing the soluble salts from the product by digestion in water. The protoxide then remains in the form of a blackish grey, metallic powder. It is anhydrous, and is reduced by hydrogen gas at ordinary temperatures. Contains 13·4 per cent. of oxygen.

| | | | | | Claus. |
|---|---|---|---|---|---|
| Ru | 52·1 | .... | 86·69 | ..... | 86·6 |
| O | 8·0 | .... | 13·31 | ..... | 13·4 |
| RuO | 60·1 | .... | 100·00 | ..... | 100·0 |

The compounds of this oxide have not been much examined. The hydrate has not yet been obtained; its preparation would probably be as difficult as that of hydrated protoxide of iron. The oxide is insoluble in acids, and consequently its salts cannot be directly formed. A soluble protochloride appears, however, to be obtained by the action of sulphuretted hydrogen and other reducing agents on the sesquichloride (p. 400).

### B. Sesquioxide of Ruthenium. $Ru^2O^3$.

Pulverulent ruthenium, strongly heated before a powerful blowpipe, turns black, and rapidly absorbs oxygen, 100 parts of the metal increasing to 118 parts; afterwards the oxidation slowly proceeds further, till the oxide acquires a blackish blue colour, and contains 23 or 24 parts of oxygen to 100 parts of metal, which is about the proportion required for the sesquioxide.

| | | | | | Claus. | | |
|---|---|---|---|---|---|---|---|
| 2Ru | 104·2 | .... | 81·16 | ..... | 81·33 | .... | 80·64 |
| 3O | 24·0 | .... | 18·84 | ..... | 18·67 | .... | 19·36 |
| $Ru^2O^3$ | 128·2 | .... | 100·00 | ..... | 100·00 | .... | 100·00 |

This oxide, when ignited for a long time, increases still further in weight, but the quantity of oxygen absorbed is never sufficient to form the bioxide.

*Combinations.*—*a.* With Water.—Hydrated Sesquioxide of Ruthenium.—1. Formed by precipitating a solution of the sesquichloride with an alkali; the precipitate requires very careful washing, but even then it retains 2 or 3 per cent. of alkali.—2. By precipitating rutheniate of potash with nitric acid (p. 401).—3. The aqueous solution of the sesquichloride is resolved by heat into free hydrochloric acid and the hydrated sesquioxide. Black-brown powder, which becomes suddenly incandescent when heated. Hydrogen gas reduces it imperfectly at ordinary temperatures. It is insoluble in alkalis.

| | | | |
|---|---|---|---|
| $Ru^2O^3$ | 128·2 | .... | 82·60 |
| 3HO | 27·0 | .... | 17·40 |
| $Ru^2O^3 + 3Aq$ | 155·2 | .... | 100·00 |

*b.* With Acids, forming the Salts of Sesquioxide of Ruthenium.—The hydrated sesquioxide dissolves in acids, forming orange-yellow solutions. A solution of this oxide in hydrochloric acid exhibits the following characters with reagents:—Sulphurous acid decolorizes it after long-continued action.—Hydrosulphuric acid partly precipitates the metal in the form of a black sulphide, and at the same time reduces the sesquichloride to protochloride, the reduction being accompanied by a change of colour from orange-yellow to a fine azure blue. This reaction affords a very delicate test of the presence of ruthenium in any of its compounds. To obtain it, the compound must be fused at a strong heat in a platinum spoon with a large excess of nitre, the heat being continued till the

ignited mass no longer froths, but fuses quietly: it is then left to cool, and dissolved in a small quantity of water. The orange-yellow solution (containing rutheniate of potash) yields, on the addition of two drops of nitric acid, a bulky black precipitate of sesquioxide of ruthenium; and on adding hydrochloric acid to the liquid, and heating it in a porcelain capsule, the precipitate dissolves, and the solution, when concentrated, assumes a fine orange-yellow colour. Lastly, on passing sulphuretted hydrogen through this solution till it becomes nearly black, and filtering, a filtrate is obtained, exhibiting the splendid blue colour above mentioned. Two milligrammes of the metal are sufficient for the production of this reaction.—Zinc likewise reduces the orange-yellow sesquichloride to the blue protochloride.—Hydrosulphate of ammonia precipitates the greater part of the ruthenium in the form of a black-brown sulphide, which is not perceptibly soluble in excess of the reagent.—Alkalis, both caustic and in the state of carbonate, immediately throw down a black-brown precipitate of sesquioxide of ruthenium, soluble in an excess of the reagent; a portion of the metal, however, remains in the solution. Phosphate of soda produces the same reaction.—Borax forms no precipitate at first, but, on heating the solution, the hydrated sesquioxide is precipitated.—Chloride of potassium and chloride of ammonium produce dark brown, crystalline precipitates, but only in very concentrated solutions.—Formiate of soda does not precipitate the metal, but merely decolorizes the solution.—Oxalic acid acts in a similar manner.—Ferrocyanide of potassium decolorizes the solution at first, but afterwards turns it blue.—Cyanide of mercury colours the solution blue, and throws down a blue precipitate.—Nitrate of silver forms a black precipitate, which afterwards turns white, the solution at the same time becoming rose-coloured. This reaction is very delicate. The black precipitate is a mixture of chloride of silver and sesquioxide of ruthenium; it dissolves partially in the course of 24 hours, the oxide of ruthenium dissolving in the free nitric acid (probably with loss of oxygen), and forming a cherry-red solution, while the chloride of silver remains behind in the form of a white residue. On adding excess of ammonia to the liquid, the chloride of silver dissolves, and black sesquioxide of ruthenium remains behind. (Compare the reaction of nitrate of silver with iridic salts, p. 392.)

### C. Bioxide of Ruthenium, or Ruthenic Oxide. $RuO^2$.

1. Formed by roasting and igniting the bisulphide.—2. By strongly igniting the bisulphate of ruthenic oxide, $RuO^2, 2SO^3$.—When prepared by (1), it forms a black-blue powder, inclining to green; by (2), small grey particles, with metallic lustre and bluish or greenish iridescence.

| | | | | Claus. |
|---|---|---|---|---|
| Ru | 52·1 | 76·50 | | 76·51 |
| 2O | 16·0 | 23·50 | | 23·49 |
| $RuO^2$ | 68·1 | 100·00 | | 100·00 |

The *Hydrate of Ruthenic Oxide* is obtained in the form of a gelatinous precipitate, when a solution of bichloride of ruthenium and potassium is mixed with carbonate of soda and evaporated. The precipitate, which retains a considerable quantity of alkali, is yellowish brown while moist; but after drying, it has the colour of impure rhodic oxide. When

heated in a platinum spoon, it deflagrates with vivid incandescence, and is scattered about. It appears to contain 2 At. water: $RuO^2 + 2Aq$.

The *Salts of Ruthenic Oxide* are obtained in the state of solution by digesting the hydrated oxide in acids. The solutions are yellow, but become rose-coloured when concentrated by evaporation.

### D. Ruthenic Acid. $RuO^3$.

Known only in combination with potash; it appears, indeed, to be a very instable compound, being easily resolved into oxygen and ruthenic oxide.

## Ruthenium and Sulphur.

A. Sulphides of Ruthenium.—Ruthenium probably forms with sulphur a number of compounds exactly corresponding to the oxides; but the preparation of these sulphides is attended with many difficulties. Pulverulent ruthenium and sulphur heated together in an atmosphere of carbonic acid, exhibit no sign of chemical combination. The sulphur distils off, and the ruthenium gains only 2 or 3 per cent. in weight. Moreover, the precipitates formed by passing sulphuretted hydrogen through the solutions of the several chlorides of ruthenium, do not correspond in composition to the chlorides from which they are produced; they always contain too much sulphur, and are in all probability mixtures of the definite sulphides with sulphur. The analysis of these compounds is very difficult. They are very apt to oxidate in drying, being thereby converted into sulphates. When they are heated, to drive off water, they explode slightly with incandescence; and when treated with fuming nitric acid, they oxidate, with emission of sparks and slight explosion. Nitric acid of ordinary strength dissolves them readily; but the precipitate produced on adding a baryta-salt to the solution, always carries down with it a certain quantity of ruthenic sulphate, which cannot be removed by any solvent whatever.

When the sulphide obtained by precipitation from the sesquichloride is heated in a bulb-tube through which carbonic acid is passed, incandescence and explosion are produced, sulphur and water pass off, and the remaining blackish grey, metallic powder, yields, on analysis, results corresponding to the formula $Ru^2S^3$.—The sulphide which is precipitated on passing sulphuretted hydrogen for a short time through a solution of the sesquichloride, often contains 3 At. sulphur to 1 At. ruthenium; but if the gas be passed through the solution for several hours, a yellowish brown sulphide is obtained, having the composition $RuS^2$. From the blue chloride, sulphide of ammonium throws down a precipitate which appears to be composed of $Ru^2S^5$.—None of these results, however, can yet be looked upon as satisfactorily established.

B. Sulphate of Ruthenic Oxide, or Ruthenic Sulphate.—$RuO^2, 2SO^3$.—When the sulphide of ruthenium obtained by treating the sesquichloride with sulphuretted hydrogen, is digested in nitric acid of ordinary strength, an orange-yellow solution is obtained, which, when evaporated to dryness, yields a yellowish brown, amorphous mass, resembling mosaic gold, when reduced to powder. It is deliquescent, has a sour, astringent taste, and dissolves readily in water. Alkalis added to

the solution do not form any precipitate at first; but, on evaporation, a yellowish brown, gelatinous precipitate is obtained, consisting of hydrated ruthenic oxide, and presenting a most striking resemblance to impure rhodic oxide. In the solution of the salt, sulphuretted hydrogen does not produce any blue reaction.

### Ruthenium and Chlorine.

Ruthenium, under certain circumstances, forms a series of chlorides, exhibiting a succession of prismatic colours, viz., green, blue, violet, purple-red, cherry-red, and orange-yellow.

A. Protochloride of Ruthenium.—RuCl.—Ruthenium, at a low red heat, is slowly attacked by chlorine, and converted into protochloride. On placing the metal in a bulb-tube, igniting it over the flame of an argand spirit-lamp, and passing dry chloride gas over it, a yellow fume (probably consisting of the highest chloride, which is volatile), is first produced and carried forward by the stream of gas, the metal at this stage not undergoing any alteration of appearance or perceptible increase of bulk; but at a later period, a small portion of sesquichloride sublimes, and the metal turns black, and in the course of two hours, is converted into a black and partly crystalline chloride. Frequently, however, the conversion is not complete in the first process, and to saturate the metal completely with chlorine, it is necessary to pulverize the product, and repeat the process. The product of this second operation always gives, on analysis, results corresponding with the above formula.

Protochloride of ruthenium obtained in the manner just described is insoluble in water and in acids; water, however, extracts from it a trace of sesquichloride. A solution of caustic potash likewise acts but slightly upon it, even when evaporated to dryness with it. When the residue of this last operation is washed with water, and then digested in hydrochloric acid, a small quantity of oxide is dissolved out, and the acid assumes the colour of the sesquichloride.

*Aqueous Protochloride of Ruthenium*, or *Hydrochlorate of Ruthenious Oxide.*—When sulphuretted hydrogen is passed for some time through a solution of sesquichloride of ruthenium, a black-brown sulphide is precipitated, and the liquid acquires the fine azure-blue colour, already mentioned (p. 398). The excess of sulphuretted hydrogen may be expelled by passing a current of air through the liquid; and the blue solution which then remains, appears to consist of protochloride of ruthenium, with excess of hydrochloric acid. The composition cannot be determined by direct analysis, because the compound is very liable to decompose and pass to the state of sesquichloride, and therefore cannot be obtained either in the solid state, or in the form of a crystalline double salt. The preceding supposition as to its constitution, is, however, rendered highly probable by the following considerations: 1. Sulphuretted hydrogen exerts a reducing action on the chlorides of other platinum metals; 2. The sulphide which is precipitated in the formation of the blue chloride contains, not 3 At. sulphur to 2 At. metal, but 2 At. sulphur, or even more, to 1 At. metal; 3. The sesquichloride is turned blue by other reducing agents, such as zinc; 4. When the solution of the sesquichloride is evaporated, and the residue heated, it turns green, and exhibits isolated blue spots; this method does not, however, yield a pure protochloride,

because part of the salt is converted into a basic compound.—Alkalis added to the solution of the blue chloride, throw down a precipitate of the sesquioxide, just as solutions of the lower chlorides of iridium, when similarly treated, yield a precipitate of bioxide of iridium (p. 373).

B. Sesquichloride of Ruthenium.—$Ru^2Cl^3$.—Formed by dissolving the sesquioxide of ruthenium (obtained by precipitation from rutheniate of potash) in hydrochloric acid, and evaporating to dryness. The residue is deliquescent, has a strongly astringent but non-metallic taste, like that of tannic acid, and dissolves in water and alcohol, forming beautiful orange-coloured solutions, but leaving a yellow basic compound undissolved. When heated, it turns green and blue, as above described. A dilute solution of the sesquichloride is resolved by heat into hydrochloric acid, and the hydrated sesquioxide (p. 397). The same change is produced in a few days at ordinary temperatures, but less completely.

| | | | |
|---|---|---|---|
| 2Ru | 104·2 | .... | 49·51 |
| 3Cl | 106·2 | .... | 50·49 |
| $Ru^2Cl^3$ | 210·4 | .... | 100·00 |

C. Bichloride of Ruthenium.—$RuCl^2$.—Not known in the separate state, but occurs in combination with chloride of potassium. It exhibits a rose-colour, similar to that of the salts of sesquichloride of rhodium.

## Ruthenium and Nitrogen.

Sesquichloride of Ruthenium and Ammonium.—Formed by mixing a strong solution of the black sesquioxide in hydrochloric acid with sal-ammoniac, and concentrating by evaporation, with addition of a small quantity of nitric acid.—Similar in form and properties to the corresponding potassium-salt. In the crystallized state, it does not dissolve readily in water, but nevertheless crystallizes with difficulty from its solutions, and only when they are concentrated. When ignited in an atmosphere of hydrogen, it leaves 32·7 per cent. of metal.

| | | | | | Claus. |
|---|---|---|---|---|---|
| 2N | 28·0 | .... | 8·83 | | |
| 8H | 8·0 | .... | 2·52 | | |
| 2Ru | 104·2 | .... | 32·85 | ..... | 32·7 |
| 5Cl | 177·0 | .... | 55·80 | | |
| $2NH^4Cl,Ru^2Cl^3$ | 317·2 | .... | 100·00 | | |

## Ruthenium and Potassium.

A. Rutheniate of Potash.—*Basic.*—Formed by igniting ruthenium with a mixture of potash and nitre or chlorate of potash. The product, when treated with water, yields a fine orange-yellow solution, having a strongly astringent taste, like that of tannic acid. This solution is neutral, provided the potash and nitre have not been added in excess. It colours organic substances black, by coating them with oxide reduced from the acid. Acids added to the solution immediately throw down a black oxide, which contains potash, if the solution has not been completely neutralized by the acid; but if the acid has been added in slight excess, the precipitated oxide contains a small quantity of acid. If sulphuric acid has been used for the precipitation and added in excess, the metal

obtained by reducing the resulting oxide contains a small quantity of sulphide of ruthenium, which is but very slowly decomposed by gentle ignition in an atmosphere of hydrogen. The precipitated oxide appears to be the hydrated sesquioxide, for it yields the sesquichloride when dissolved in hydrochloric acid.

B. Sulphite of Ruthenious Oxide and Potash.—Sulphurous acid exerts but little action upon sesquichloride of ruthenium and potassium at ordinary temperatures. When its aqueous solution is poured upon the pulverized salt, scarcely anything is dissolved, but the salt becomes cream-coloured on the surface. When the solution of the double chloride is heated with sulphite of potash, it does not lose its colour, but assumes a deeper red tint, and deposits a small quantity of a cream-coloured, pulverulent precipitate. On evaporating to dryness, redissolving and again evaporating, a further quantity of the same precipitate is thrown down, the liquid all the while retaining a deep orange-colour.

| | | | | Claus. |
|---|---|---|---|---|
| KO | 47·2 | 27·52 | | 27·54 |
| Ru | 52·1 | 30·37 | | 29·21 |
| O | 8·0 | 4·71 | | 5·01 |
| $2SO^2$ | 64·0 | 37·40 | | 38·24 |
| $KO,SO^2 + RuO,SO^2$ | 171·3 | 100·00 | | 100·00 |

When the evaporation and re-solution are very often repeated, a nearly white precipitate is at length obtained, which probably corresponds in composition to the white salts of the other platinum-metals (pp. 321, 384); but the quantity obtained was too small for analysis.

C. Sesquichloride of Ruthenium and Potassium.—The preparation of this compound has already been described (p. 395). It forms a crystalline powder, which has a brown colour with a play of violet, and when examined by the microscope, appears to be composed of small, shining, orange-yellow, transparent cubes, $\frac{1}{100}$ of a line in diameter. When reduced to a finer state of division by trituration, it assumes a yellowish brown colour. Its taste is bitter, but not metallic. It is somewhat sparingly soluble in cold water; more readily in boiling water; insoluble in alcohol of 80 per cent., resembling in this respect the corresponding salts of the other platinum-metals. Nevertheless, the salt is but partially precipitated by alcohol from a concentrated aqueous solution. Moreover, when a solution of this salt, mixed with the chloride of another metal, which is soluble in alcohol, is evaporated to dryness, and the residue digested with strong alcohol, a quantity of the ruthenium salt is dissolved, greater in proportion to that of the other chloride present. This property is likewise possessed by those double chlorides of other platinum metals which are difficultly soluble in alcohol, *e. g.*, the sesquichloride of rhodium and sodium. Crystallized sesquichloride of ruthenium and potassium is nearly insoluble in a concentrated solution of sal-ammoniac, which solution may therefore be advantageously used to wash it and free it from chloride of potassium, the sal-ammoniac itself being afterwards removed by alcohol, in which it is very soluble.

A neutral aqueous solution of this salt decomposes very readily, especially when heated, becoming darker, and finally black and opaque, and depositing a black bulky precipitate, probably a basic compound, while the liquid still remains turbid and dark-coloured. The presence of free acid prevents the decomposition. In the decomposed state just

described, the salt has an uncommonly strong colouring power, in consequence of the extremely minute division of the precipitate, which remains floating in the liquid and colours it. A milligramme of the salt dissolved in 4 grammes of water forms at first a slightly yellow-coloured liquid; but on heating this solution, it becomes as black as ink, and may then be diluted with 30 grammes of water, without much diminution of intensity. Now the salt contains only 28·9 per cent. of ruthenium; hence 1 part of that metal is capable of imparting to more than 100,000 parts of water, a colour almost as deep as that of a pale ink; the colour, however, inclines somewhat to brown. Ammonia added to a solution of the double chloride throws down a black precipitate, which contains chlorine and ammonia, and, when dissolved in hydrochloric acid and afterwards evaporated to dryness, yields a dingy green, saline mass. On dissolving this mass in water, an opaque, blackish cherry-red liquor is obtained, which, when mixed with a small quantity of nitric acid and evaporated, assumes a succession of tints, passing through violet, blue, purple-red, cherry-red, brown, and finally becoming orange-yellow.

| | | | | Claus. | | |
|---|---|---|---|---|---|---|
| 2K | 78·4 | 21·80 | | 21·45 | 21·71 | 21·59 |
| 2Ru | 104·2 | 28·97 | | 28·96 | 28·48 | 28·91 |
| 5Cl | 177·0 | 49·23 | | 49·59 | 49·82 | 49·53 |
| $2KCl,Ru^2Cl^3$ | 359·6 | 100·00 | | 100·00 | 100·01 | 100·03 |

The potassium was estimated as chloride, and the chlorine in combination with the ruthenium estimated by loss. Direct determinations of this portion of chlorine by precipitation with nitrate of silver gave results more than 1 per cent. too low, showing that the salt contained water.—It was from the analysis of this salt that the atomic weight of ruthenium was first determined.

D. Bichloride of Ruthenium and Potassium.—$KCl; RuCl^2$.—Formed by treating the salt C with aqua-regia, or with a mixture of hydrochloric acid and chlorate of potash. With aqua-regia the conversion is very slow and incomplete; and when the mixture of hydrochloric acid and chlorate of potash is used, the greater part of the ruthenium is converted into a volatile chloride (probably $RuCl^3$), which passes off with the watery vapour. The salt was once obtained accidentally on precipitating the oxide of ruthenium from a solution of rutheniate of potash, with a quantity of nitric acid larger than necessary. The filtered liquid was brown, and when mixed with a little hydrochloric acid and evaporated, yielded at first a large quantity of nitre; but on further evaporating the rose-coloured mother-liquid, a red salt crystallized out, which, when washed, first with sal-ammoniac, and then with alcohol, proved to be the compound D in a state of purity.

The crystals of this salt are so small, that their form cannot be distinguished with the naked eye; but when magnified 300 times (in linear dimension), they are seen to be perfectly transparent, rose-coloured prisms, with acuminated summits, and apparently belonging to the rhombohedral system. The salt is easily soluble in water, insoluble in alcohol of 70 per cent., and dissolves very sparingly in a concentrated solution of sal-ammoniac. Its solution is rose-coloured, with a play of violet, and is undistinguishable in appearance from that of the sesquichloride of rhodium and sodium. Sulphuretted hydrogen affects it but slightly, the liquid, after a while, depositing a small quantity of brown sulphide, but without losing its red colour, or exhibiting any trace of the blue reaction, which is produced, under similar circumstances, in solutions of the sesqui-

chloride. Alkalis added to a solution of the salt produce no immediate precipitate, but the liquid, when evaporated, deposits a yellowish brown hydrated oxide, which contains a large quantity of alkali, and when heated in a platinum spoon exhibits sudden incandescence, attended with slight explosion. A concentrated aqueous solution of the salt is but partially precipitated by alcohol, the greater part remaining dissolved in the liquid, which retains its rose colour. The solution is not reduced to the state of a lower chloride by evaporation.

| | | | |
|---|---|---|---|
| K | 39·2 | .... | 19·85 |
| Ru | 52·1 | ... | 26·37 |
| 3Cl | 106·2 | .... | 53·78 |
| $KCl,RuCl^2$ | 197·5 | .... | 100·00 |

### Ruthenium and Sodium.

*Sesquichloride of Ruthenium and Sodium?*—This compound was not obtained in a definite crystalline form, and therefore could not be accurately analysed. It forms a semi-crystalline, deliquescent mass, easily soluble in alcohol. When strongly heated, it dried up, but at the same time turned partly green and blue, behaving, in fact, like a mere mixture of common salt and sesquichloride of ruthenium.

### Ruthenium and Barium.

*Sesquichloride of Ruthenium and Barium?*—A solution containing a mixture of chloride of barium and sesquichloride of ruthenium, behaves like the sodium-salt. Alcohol extracts the chloride of ruthenium from it, and leaves the chloride of barium undissolved.

Ruthenium likewise combines with iridium and osmium, the compound existing, in fact, in platinum ore. ¶

## Chapter XLIV.

# OSMIUM.

For the *Literature*, vid. *Iridium;* also

Fritzsche & Struve.—Osmiamic Acid (Osman-Osmiumsäure), *J. pr. Chem.* 41, 97; abstr. *Ann. Pharm.* 64, 263; *Jahresber. L & K*, 1847—8, 461; also, with observations by Gerhardt; *Compt. rend. trav. chim.*, 1847, 304.

*History*, vid. *Iridium.*

*Sources.* The same as for iridium, with the exception of (3) p. 369.

*Preparation.* Vid. *Analysis of Platinum ore* (pp. 258, 259, No. 18—26; pp. 262—264, No. 23—28; pp. 265, 266, No. 23—28; p. 266, No. 2; pp. 268—270, No. 1—5; p. 270, No. 1—6; p. 271, *c*).—1. By heating sesquichloride of osmium and ammonium (previously mixed with at least one-third of its weight of sal-ammoniac, to prevent intumescence) in a retort, till the bottom of the retort becomes red-hot, and no more sal-ammoniac passes over. (Berzelius, p. 263, No. 28, *β*.)—2. By causing heated osmic acid to volatilize in a current of hydrogen gas, and passing the gaseous mixture through a tube, one part of which, an inch in length, is kept at a red heat; at that part, the osmium is deposited in the form of a compact ring. (Berzelius.)—3. Aqueous osmic acid mixed with hydrochloric acid, is precipitated by mercury, and the precipitate heated in an atmosphere of hydrogen. (Berzelius, p. 263, No. 28.)—4. Or it is precipitated by zinc. (Vauquelin, p. 259, No. 26.)

*Properties.* By (1): Loosely coherent, porous mass, having a blue greyish white colour and strong metallic lustre.—By (2): Compact mass, in thin laminæ slightly flexible and elastic; has the lustre of osmide of iridium, and a specific gravity of about 10·0. In the perfectly coherent state, however, it would probably be much heavier; vid. *Osmide of Iridium.*—By (3): Black powder, which acquires the metallic lustre when pressed, and has a density of about 7·6. (Berzelius.)—By (4): Black powder, which, under the burnishing steel, acquires metallic lustre and the colour of copper. (Vauquelin.)—Does not fuse or volatilize, when heated to whiteness in a hollow in a piece of charcoal. (Tennant.)

### *Compounds of Osmium.*

Most compounds of osmium may be recognized by their property of giving off osmic acid, when heated on platinum-foil before the blowpipe

with a small quantity of carbonate of soda; the osmic acid may be known by its odour, and by the luminosity which it imparts to the flame of alcohol. (Berzelius.)

## Osmium and Oxygen.

### A. Protoxide of Osmium, or Osmious Oxide. OsO.

Obtained by gently igniting the hydrate of osmious oxide in a close vessel. (Berzelius).

| | | | |
|---|---|---|---|
| Os | 99 | .... | 92·52 |
| O | 8 | .... | 7·48 |
| OsO | 107 | .... | 100·00 |

(OsO = 1244·487 + 100 = 1344·487. Berzelius.)

Hydrate of Osmious Oxide.—The aqueous solution of protochloride of osmium and potassium, gradually becomes turbid on being mixed with potash, and after a few hours deposits a greenish black hydrate of osmious oxide, which, however, contains a quantity of potash not to be extracted by water. The filtrate contains a small quantity of osmious oxide in solution, which gives it a greenish yellow colour. The hydrate heated to commencing redness in close vessels, gives off its water without any osmic acid; when heated with combustible bodies, it detonates, and yields reduced osmium. When immersed in hydrogen gas at ordinary temperatures, it becomes heated, and yields water and metallic osmium. (Berzelius.)

Osmious Salts.—The hydrate dissolves in acids slowly but completely forming blackish green solutions. (Berzelius.)

### B. *Sesquioxide of Osmium?* $Os^2O^3$.

Not known in the separate state.

| | | | |
|---|---|---|---|
| 2Os | 198 | .... | 89·19 |
| 3O | 24 | .... | 10·81 |
| $Os^2O^3$ | 222 | .... | 100·00 |

($Os^2O^3$ = 2 · 1244·487 + 300 = 2788·973. Berzelius.)

The solutions of ammonio-sesquioxide of osmium in acids are yellowish brown, or when nearly saturated, black-brown.—On mixing the aqueous solution of sesquichloride of osmium and potassium with potash, it assumes a fine purple-brown colour; after digestion for some time, it deposits the hydrated protoxide, while teroxide of osmium remains dissolved and imparts a rose-colour to the liquid. (Berzelius.)

*Blue Oxide of Osmium.*—Osmium ignited in a retort containing air, first yields a white sublimate of osmic acid, and afterwards a blue sublimate, which appears green by transmitted light. (Vauquelin.) This blue sublimate, which is insoluble in water, is likewise obtained on heating platinum ore in a retort. (Descotils.) Tincture of galls forms a blue liquid with aqueous osmic acid. (Tennant.)—Sulphurous acid forms with

aqueous osmic acid, a blue liquid, which may be regarded as sulphate of blue oxide of osmium. This blue oxide is perhaps a mixture of protoxide and sesquioxide, or of protoxide and bioxide of osmium. (Berzelius.)

### C. Bioxide of Osmium, or Osmic Oxide. $OsO^2$.

*Preparation.* 1. When bichloride of osmium and potassium is heated with dry carbonate of soda in a retort to a temperature somewhat below redness, till the evolution of carbonic acid ceases (a small quantity of osmic acid, formed by the air in the apparatus, volatilizing at the same time), and the residue exhausted with water and hydrochloric acid, pure osmic oxide remains behind.—2. The same compound is formed by heating the dried hydrate of osmic oxide in an atmosphere of carbonic acid, a small quantity of osmic acid being likewise given off after the water has escaped. (Berzelius.)

Black powder.—When kept from contact of air, it sustains a red heat without decomposition. Hydrogen gas reduces it at ordinary temperatures. It detonates when heated with combustible bodies. (Berzelius.)

| | | | |
|---|---|---|---|
| Os | 99 | .... | 86·09 |
| 2O | 16 | .... | 13·91 |
| $OsO^2$ | 115 | .... | 100·00 |

($OsO^2 = 1244{\cdot}487 + 200 = 1444{\cdot}487$. Berzelius.)

Hydrate of Osmic Oxide.—A saturated aqueous solution of bichloride of osmium and potassium mixed with a small quantity of carbonate of potash or soda, exhibits no change at first, but gradually acquires a black turbidity, and deposits black hydrated osmic oxide, which must be freed from adhering potash by hydrochloric acid.—The filtrate is pale yellow.—If too much carbonate of potash be added, the greater part of the oxide remains dissolved, forming a dark brown solution, from which, however, it separates slowly when left at rest, and immediately on boiling, the separation in either case being almost complete. (Berzelius.)

Osmic Salts.—Osmic oxide and its hydrate are insoluble in acids, hydrochloric acid alone colouring them yellow after long digestion. Osmic salts obtained by other processes are brownish yellow.

### D. *Teroxide of Osmium, or Osmious Acid?* $OsO^3$.

This oxide is supposed by Berzelius to exist in the rose-coloured alkaline liquid (p. 406), which is produced, accompanied by precipitation of the protoxide, on digesting an aqueous solution of sesquichloride of osmium and potassium mixed with potash.

### E. Osmic Acid. $OsO^4$.

*Formation.* 1. Osmium does not oxidize in the air either at ordinary temperatures or at 100°; at higher temperatures, however, oxidation takes place. In the finely divided state, as it is obtained by reduction with mercury or formic acid, it may be set on fire, and then continues to glow; in the more compact state, it ceases to burn as soon as it is taken out of the fire. The lower oxides of osmium, when heated in the air, are converted into osmic acid and volatilize. (Berzelius.)—2. Osmium

which has been strongly ignited, is insoluble in nitric acid, aqua-regia and other acids; that which has been less strongly ignited is slowly dissolved by moderately strong nitric acid, in the form of osmic acid, which passes over when the liquid is distilled; it dissolves more readily in aqua-regia, and with yet greater facility in hot concentrated nitric acid. Osmic acid is likewise formed when the lower oxides of osmium, or the compounds of chloride of osmium with other metallic chlorides, are heated with nitric acid; also when vapour of chloride of osmium mixed with chlorine gas is passed into milk of lime. (Berzelius.)—3. When osmium is ignited with hydrate of potash in contact with the air, or with addition of nitre.

*Preparation.* 1. By slowly passing oxygen gas over osmium heated to redness in the first of two bulbs blown on a glass tube. The greater part of the osmic acid then collects in the second bulb, which must be kept cool; 2 or 3 per cent. is carried further with the oxygen gas, which should therefore be passed through ammonia or potash. (Berzelius.)—2. By Wöhler's process (p. 269, No. 3.)—3. By keeping an intimate mixture of 3 parts of osmide of iridium and 1 part of nitre at a strong red heat in an earthen crucible, till the mass becomes pasty, and vapours of osmic acid are evolved—dissolving the product, when cold, in the smallest possible quantity of water—mixing the solution in a retort with a quantity of sulphuric acid (formed of equal parts of oil of vitriol and water) sufficient to neutralize the potash—and distilling rapidly, as long as osmic acid continues to pass over. The osmic acid coats the receiver with a white crust, and afterwards fuses in drops at the bottom of the watery liquid. (Wollaston, *Schw.* 57, 827; also *Pogg.* 16, 167.)

*Properties.* Sublimes in colourless, transparent, shining needles; solidifies, after fusion, in a white, translucent, crystalline mass, which, at the temperature of the hand, may be bent like wax. (Vauquelin.) Fuses more easily than wax into an oily liquid. (Vauquelin.) Boils and evaporates without decomposition at a moderate heat. A slight rise of temperature causes it to sublime in needles from one part to the other of the vessel in which it is kept. (Wöhler, *Pogg.* 31, 164.) Does not redden litmus when dissolved in water. (Tennant, Vauquelin.)—Its taste is acrid and burning, like that of oil of cloves. (Vauquelin.) Sweetish. (Tennant.) Has an insupportably pungent odour, resembling that of chlorine or iodine. (Vauquelin.) Air containing vapour of osmic acid, attacks the lungs strongly when inhaled, producing long-continued expectoration, and excites a burning pain in the eyes. (Berzelius.) Even extremely small quantities of the vapour act violently on the eyes and lungs. (Wöhler.)—¶ As a remedy for poisoning by osmic acid, Claus recommends the *immediate* inhalation of sulphuretted hydrogen.¶—Osmic acid blackens all organic substances, even the cuticle, by reduction of osmium, especially when they are wet. (Tennant, Vauquelin.)

| | | | |
|---|---|---|---|
| Os | 99 | .... | 75·57 |
| 4O | 32 | .... | 24·43 |
| $OsO^4$ | 131 | .... | 100·00 |

($OsO^4 = 1244·487 + 400 = 1644·487$. Berzelius.)

*Decompositions.* 1. Osmic acid may be sublimed without decomposition in hydrogen gas; but if the hydrogen mixed with the vapour be

passed through a tube heated to redness at one point, the reduction of the osmium takes place at that point, without explosion, and does not extend to the colder parts of the mixture. Osmic acid is likewise reduced by an alcohol-flame. If therefore a granule of osmium be placed on the edge of a piece of platinum foil, and held in the flame of a spirit-lamp, in such a manner as to allow part of the flame to rise freely into the air, this part becomes brightly luminous,—because the osmic acid formed by the combustion of the osmium mounts upwards, and is again reduced by the flame to metallic osmium, which thus mixes with the flame, as a finely divided solid body, and thereby increases the luminosity (II., 29). (Berzelius.)—2. The acid deflagrates on glowing coals, like nitre. (Thénard.) —3. Phosphorus reduces the metal from the aqueous solution. (Tennant, Fischer.)—4. The osmium is reduced to the metallic state from the aqueous solution of the acid, by nearly all the metals, even by mercury, which forms an amalgam, and by silver, which acquires a black coating, but not by gold, platinum, rhodium, or iridium. (Tennant.)—From the pure aqueous solution, metals precipitate but a small quantity of osmium, together with an osmiate of the metallic oxide, but from an acidulated solution they precipitate the whole. (Berzelius.) Zinc, cadmium, tin, and iron, throw down the osmium from the acidulated solution in the form of a blue or reddish black powder, which remains for a long while suspended in the liquid, and gives it a blue colour; on antimony, bismuth, lead, copper, mercury, and silver, on the contrary, the osmium is immediately deposited as a solid crust, and does not impart any blue colour. If the zinc is in contact with platinum, the osmium is deposited in the form of a reddish grey film on the glass in the neighbourhood of the platinum. Lead effects an incomplete reduction, and finally throws down a white powder. Silver immersed in the liquid becomes covered with various tints, and ultimately turns black; this effect taking place even in solutions which are so dilute as scarcely to give off any odour. Silver thus tarnished does not lose its coating of osmium till it is heated in the air nearly to redness. (Fischer, *Pogg.* 12, 499.)—5. Green vitriol reduces osmium from the aqueous solution; protochloride of tin has no action upon it. (Fischer.)—6. The dry acid is decomposed by sulphuretted hydrogen, yielding sulphide of osmium and water; the action takes place even in the cold, and is attended with rise of temperature. (Berzelius.) —7. The aqueous acid treated with a small quantity of sulphurous acid, turns yellow (probably from formation of sulphate of osmic oxide); a larger quantity turns it brown (probably from sulphate of the sesquioxide); a still larger quantity, green; and a still further addition gradually turns it deep blue (sulphate of the blue oxide). (Berzelius.)—8. The solution of osmic acid in a large excess of aqueous ammonia blackens slowly in the cold, but in a few hours when heated, nitrogen gas being slowly evolved, and ammonio-sesquioxide of osmium deposited in the form of a transparent, yellowish brown film. (Berzelius.)—9. The colourless solution of osmic acid in alcohol or ether deposits all the osmium in the metallic state in the course of a few hours. Osmic acid dissolved in water is not decomposed by alcohol or ether; but tallow or oil effects the decomposition. (Berzelius.) Tincture of galls colours the aqueous solution purple at first, and afterwards dark blue, by formation of the blue oxide. (Tennant.)

*Combinations.* *a.* With Water.—Aqueous Osmic Acid.—The acid dissolves readily in water. (Vauquelin.) It dissolves very slowly, even

at the temperature at which it melts. (Berzelius.) Transparent and colourless solution, which has the taste and smell of the acid.

*b.* With Acids.—The mixture of osmic acid with the aqueous solutions of the stronger mineral acids is yellowish red, smells of osmic acid, and gives it off when distilled.

*c.* With Salifiable Bases, forming salts called Osmiates. Aqueous osmic acid does not expel carbonic acid from the alkaline carbonates. (Berzelius.) The dry alkaline osmiates are yellowish red; the aqueous solutions, yellow; they do not emit any odour of osmic acid, and give off that acid but partially when boiled. Even when osmiate of potash or soda is heated to redness, a large quantity of osmic acid remains behind. According to Frémy (*Compt. rend.* 18, 1110), the alkaline osmiates yield with sulphurous acid, peculiar compounds, in which the properties of the sulphurous acid are masked.

## Osmium and Phosphorus.

A. Phosphide of Osmium.—Osmium ignited in phosphorus-vapour, takes it up, and becomes incandescent. After strong ignition, the compound is white and exhibits the metallic lustre; after very slight ignition, it is black, and acquires the metallic lustre by pressure. Sometimes takes fire spontaneously in the air, burns without flame or odour of osmic acid, and is converted into phosphate of osmious oxide. (Berzelius.)

B. Phosphate of Osmious Oxide, or Osmious Phosphate.—*a.* Formed by the combustion of phosphide of osmium. Dissolves partially in cold nitric acid, forming a green solution; with hot nitric acid it forms osmic acid.—*b.* By treating the hydrated protoxide with aqueous phosphoric acid. Dark blue-green, difficultly soluble in water. (Berzelius.)

## Osmium and Sulphur.

When osmium and sulphur are heated together in a retort, the osmium burns brightly in the sulphur vapour, and forms sulphide of osmium. (Berzelius.) Sulphuretted hydrogen precipitates sulphide of osmium from the hydrochloric acid solutions of all the oxides of osmium; from the rose-coloured solutions, however, (those, namely, which contain the teroxide) the precipitation takes place but slowly. All the sulphides of osmium thus obtained are dark yellowish brown, and dissolve sparingly in water, forming deep yellow solutions; they dissolve readily in nitric acid, forming sulphate of the protoxide if the sulphide of osmium is in excess, but if an excess of warm nitric acid be used, osmic acid is given off, and sulphate of the bioxide is produced. (Berzelius.)

A. Bisulphide of Osmium.—$OsS^2$.—Aqueous bichloride of osmium and potassium forms with sulphuretted hydrogen, a dark yellowish brown precipitate, which dissolves slightly in water, forming a yellow or reddish yellow solution. In aqueous caustic alkalis it does not dissolve more freely than in water, and after drying is completely insoluble in them. (Berzelius.)

B. Five-halves Sulphide of Osmium.—$OsS^2$,$OsS^3$.—Formed by igniting the tetrasulphide in vacuo. Contains 39·4 parts ($2\frac{1}{2}$ At.) sulphur

to 99 pts. (1 At.) osmium. By ignition in an atmosphere of hydrogen, it is very slowly reduced to the metallic state. The hydrogen, even after it has passed over the ignited substance for two hours, still contains a small quantity of hydrosulphuric acid. (Berzelius.)

C. Tersulphide of Osmium.—$OsS^3$.—The rose-coloured solutions of teroxide of osmium are precipitated by sulphuretted hydrogen, only when they are first saturated with it, and then set aside for some time in a closed vessel at a temperature between 50° and 70°. If the solution is very dilute, or if it is mixed with any other, it retains its rose-colour even when thus treated; and when it is evaporated, the sulphuretted hydrogen escapes. (Berzelius.)

D. Tetrasulphide of Osmium.—$OsS^4$.—Aqueous osmic acid is immediately coloured black-brown by sulphuretted hydrogen, but does not yield a precipitate till an acid is added to it, in which case the liquid becomes completely decolorized. The brown-black precipitate becomes black when dry. When ignited in a distillatory apparatus exhausted of air, it gives off sulphur, and then, at a certain temperature, exhibits incandescence, decrepitates, acquires a grey colour and metallic lustre, and is converted into B, the change not being accompanied with evolution of any permanent gas. It is insoluble in caustic alkalis, alkaline carbonates, and alkaline hydrosulphates.

E. Sulphate of Osmious Oxide, or Osmious Sulphate.—Formed by dissolving sulphide of osmium in an insufficient quantity of nitric acid, or hydrated osmious oxide in sulphuric acid. Dark brownish-green solution, which, when evaporated, leaves a dark greyish brown mass with dendritic excrescences. This residue is easily soluble in water and alcohol. The aqueous solution is precipitated by carbonate of ammonia, potash, or soda, with which, on evaporation, it yields a greenish brown, efflorescent residue which remains dry. When carbonate of ammonia is used, the residue yields by distillation water and sulphite of ammonia, and leaves grey metallic-looking sulphide of osmium. (Berzelius.)

F. Sulphate of Blue Oxide of Osmium.—When an aqueous solution of osmic acid is mixed with excess of sulphurous acid, and the dark blue liquid evaporated, the excess of sulphurous acid escapes, and there remains a dark blue, fissured, but rather soft mass, which appears copper-coloured when perfectly dry. The residue, when heated, first gives off water, then osmic acid, and lastly, a large quantity of blue sublimate, containing a considerable amount of sulphuric acid, and, after being heated to full redness, leaves metallic osmium, having a bluish white metallic lustre, and the form of the original substance. The ammonia placed in the receiver first becomes yellow by absorbing osmic acid, and afterwards purple brown, because a considerable quantity of the blue sublimate likewise passes into it; when evaporated, it assumes a dark brown colour, and leaves a dark brown saline mass, which appears to contain sulphate of sesquioxide of osmium. The washed and dried blue residue, heated in hydrogen gas, yields water, sulphuric acid, sulphuretted hydrogen, and finally a large quantity of blue sublimate, leaving a residue of osmium combined with a small quantity of sulphur. The blue residue, when thoroughly dried, is no longer soluble in water, which, however, becomes blue by

contact with it, and likewise acid by taking up the excess of sulphuric acid. The undissolved portion, washed with water and then exposed to the air in the moist state, again imparts a blue colour to a fresh portion of water. Before drying, the blue salt is soluble in caustic alkalis and alkaline carbonates; from this solution it is, for the most part, precipitated by hydrochloric acid, but the supernatant acid liquid remains brown from the presence of sesquichloride of osmium. (Berzelius.) From the blue solution mixed with hydrochloric or sulphuric acid, iron does not precipitate all the osmium, so that the liquid remains of a darker green colour than an iron solution, and the precipitated osmium, if washed and dried, and then heated in an atmosphere of hydrogen, gives off water, a small quantity of blue sublimate and hydrosulphuric acid; it therefore retains a small quantity of sulphuric acid. (Berzelius.)

A blue sublimate is likewise formed when osmium containing sulphur is heated in oxygen gas; it is less volatile than the osmic acid formed at the same time, and nearly insoluble in water;—also when osmide of iridium is fused in a distillatory apparatus with bisulphate of potash; this blue sublimate, however, contains so much acid that it dissolves in water. (Berzelius.)

G. Sulphate of Osmic Oxide, or Osmic Sulphate.—Formed by dissolving bisulphide of osmium in excess of cold nitric acid, and evaporating. A small quantity of osmic acid volatilizes at the same time.—Dark yellowish brown syrup, which dissolves in water, and forms a brownish yellow solution. The solution reddens litmus strongly; its taste is neither acid nor metallic, but bitter. It becomes somewhat paler when mixed with sulphurous acid, but does not turn blue. It is precipitated by alkalis, and forms with chloride of barium a yellow precipitate containing osmic oxide.

[Vauquelin did not succeed in causing osmium to combine with iodine, by heating the two together in a glass tube.]

## Osmium and Chlorine.

A. Protochloride of Osmium.—Chlorine gas does not act upon cold osmium; but when dry chlorine is passed over the metal heated in a long tube, protochloride of osmium is first produced, in the form of a dark green sublimate, and afterwards, at a greater distance from the osmium, a red sublimate of the bichloride.—Protochloride of osmium, if exposed to the air,—in which case it absorbs moisture,—or if prepared with moist chlorine gas, forms dark green needles. It dissolves in a very small quantity of water, forming a beautiful green liquid, which, on the addition of more water, suddenly becomes opaque and gradually filled with green, woolly particles of osmium; a still larger quantity of water decomposes it immediately, osmium being precipitated in blue flakes, while hydrochloric acid and osmic acid remain in the liquid. (Berzelius.)

| | | | |
|---|---|---|---|
| Os | 99·0 | .... | 73·66 |
| Cl | 35·4 | .... | 26·34 |
| OsCl | 104·4 | .... | 100·00 |

B. *Sesquichloride of Osmium?*—Known only in combination with sal-ammoniac. Appears to possess a brown or purple-red colour. Thus,

when a saturated aqueous solution of osmic acid is mixed with hydrochloric and mercury, and the mixture set aside till the odour has disappeared, and the liquid is evaporated in vacuo over oil of vitriol, there remains a shining purple varnish which has a metallic taste, blackens the skin, softens when exposed to the air, and dissolves in water and alcohol. The aqueous solution mixed with alkalis forms at first a clear mixture, which on digestion at a gentle heat, deposits black oxide of osmium. (Berzelius.)

C. Bichloride of Osmium.—When chlorine gas is passed over heated osmium, this compound is produced in the form of a dense cloud which condenses to a red powder. If the chlorine gas was moist, or if the bichloride of osmium be exposed to the air, it is first converted into a transparent yellow film, then into a dark vermillion-coloured mass, which does not fuse at the heat of the hand, and, in the further part of the tube, into yellow laminæ and needles united in stellate groups, which melt at the heat of the hand, are probably richer in water than the red crystals, perhaps also contain a different proportion of chlorine.—Bichloride of osmium dissolves in a small quantity of water, forming a yellow solution, which turns green when mixed with a large quantity of water, then becomes quickly opaque, and is decomposed with complete loss of colour, like the solution of protochloride of osmium. (Berzelius.)

D. *Terchloride of Osmium?*—Known only in combination with sal-ammoniac.

E. Hydrochlorate of Osmic Acid.—Formed by mixing aqueous osmic acid with hydrochloric acid, or by dissolving osmium in aqua-regia, a large quantity of osmic acid, however, volatilizing, even at ordinary temperatures. Yellowish red liquid, which smells of osmic acid. A zinc plate immersed in it first produces a beautiful blue colour, and afterwards precipitates the osmium in black flakes. The dilute solution is coloured blue by tincture of galls. (Vauquelin.)

## Osmium and Nitrogen.

¶ A. Osmiamic Acid.—$Os^2NO^5$ according to Gerhardt; or $Os^2NO^4$, according to Fritzsche & Struve.—*Formation.* By the action of ammonia on osmic acid.—When caustic ammonia is added to a solution of osmic acid in excess of potash, the deep orange colour of the liquid soon changes to light yellow, and a new salt is produced, which separates in the form of a yellow crystalline powder, sometimes immediately, sometimes on evaporating the liquid at a gentle heat. The presence of potash, or any other metallic oxide, is not absolutely necessary to the formation of the new acid; but the ammoniacal salt which is formed when ammonia alone is added, is very liable to change, and decomposes during evaporation. Fritzsche & Struve, who discovered this new compound, assign to it the formula $OsN,OsO^4$; regarding it as a compound of nitride of osmium OsN (to which they give the name of *Osman*) with osmic acid; hence they call it *Osman-osmic acid* (*Osman-Osmiumsäure*). Gerhardt, on the contrary, regards it as a compound of 2 At. osmium, 1 At. nitrogen, and 5 At. oxygen, its formation taking place in the manner represented by the equation,

$$2OsO^4 + NH^3 = 3HO + Os^2NO^5.$$

If Fritzsche and Struve's formula were correct, the formation of the acid would be attended with evolution of 1 At. oxygen; but they particularly observe that no escape of gas takes place. On the other hand, it must be admitted that the formula $Os^2NO^4$, accords better with the analyses made by Fritzsche & Struve, than that which Gerhardt assigns to the compound.

Osmiamic acid is not known in the separate state.

| *Calculation,* according to Fritzsche & Struve. | | | *Calculation,* according to Gerhardt. | | |
|---|---|---|---|---|---|
| $Os^2$ | 198 | 81·14 | $Os^2$ | 198 | 78·57 |
| N | 14 | 5·74 | N | 14 | 5·56 |
| $O^4$ | 32 | 13·12 | $O^5$ | 40 | 15·87 |
| $Os^2NO^4$ | 244 | 100·00 | $Os^2NO^5$ | 252 | 100·00 |

*Combinations.* *a.* With Water.—Aqueous Osmiamic Acid.—Obtained by cautiously adding sulphuric acid to a solution of osmiamate of baryta, or by decomposing recently prepared and still moist osmiamate of silver with dilute hydrochloric acid. The filtered liquid, which is of a light yellow colour, may be preserved without alteration for some days, provided it be sufficiently dilute; but in the contrary case, it turns brown and decomposes, giving off gas and osmic acid, and depositing a black, non-explosive substance containing osmium. The same change takes place when a dilute solution of the acid is left to evaporate over oil of vitriol.

Osmiamic acid is a powerful acid; it not only disengages carbonic acid from carbonates, but likewise decomposes chloride of potassium; thus, when a drop of aqueous acid is left to evaporate on a glass plate in contact with a crystal of chloride of potassium, crystals of osmiamate of potash are obtained.—Metallic zinc dissolves in the aqueous acid, causing a slight evolution of gas; part of the acid is, at the same time decomposed, and the zinc becomes covered with a closely adhering, black deposit, while portions of flocculent matter become diffused through the liquid, which at the same time acquires the odour of osmic acid. The action stops, as soon as all the non-decomposed acid is saturated with zinc.—Acids at ordinary temperatures exert no decomposing action on aqueous osmiamic acid, but on the application of heat, the liquid turns brown, and gives off osmic acid. The products of decomposition vary according to the nature of the acid.

*b.* With Salifiable Bases, forming salts called Osmiamates.—These salts are formed: 1. By the direct action of osmic acid on an ammoniacal solution of the bases (in this way the potash, zinc, and silver-salts are formed).—2. By precipitating a solution of osmiamate of potash with various metallic salts.—3. By decomposing the silver-salt with metallic chlorides.—They are anhydrous. When heated, they are decomposed, with explosion, the products of the decomposition being metallic osmium, an osmiate of the base, and an osmic compound containing less oxygen. In many of these salts, the same decomposition is produced by percussion. Osmiamate of mercurous oxide, however, volatilizes without explosion when suddenly heated, and gives off an odour of osmic acid. Most of the osmiamates are affected by acids, in a similar manner to aqueous osmiamic acid. [For the action of hydrochloric acid on osmiamate of potash, see p. 420.]

Aqueous osmiamic acid and the soluble osmiamates give a dirty yellow, non-crystalline precipitate with acetate of lead, light yellow with mercu-

rous nitrate, and a lemon-yellow, crystalline precipitate with nitrate of silver. (Fritzsche & Struve.) ¶

B. Nitrate of Osmious Oxide, or Osmious Nitrate.—The hydrated prooxide dissolves in cold nitric acid, forming a green solution, which, if saturated, dries up on evaporation to a green, transparent varnish. (Berzelius.)

C. Ammonio-sesquioxide of Osmium.—To form this compound, osmic acid is dissolved in excess of strong aqueous ammonia, and the reddish yellow mixture kept for a while in a stoppered bottle at a temperature between 40° and 60°, till it acquires a black-brown colour, and the ammonio-sesquioxide of osmium begins to precipitate; the bottle may then be opened, as the evolution of osmic acid is at an end, and the nitrogen gas would otherwise be unable to escape. The decomposition takes place slowly in the cold, but in two hours if aided by heat. The dark liquid, which holds the greater part of the compound in solution, is finally evaporated in an open vessel, till all the free ammonia has escaped, and the black precipitate is washed upon a filter.—Brown-black powder.—When heated after drying, it decomposes with a hissing noise, nitrogen and aqueous vapour being evolved, the osmium reduced to the metallic state, and the mass blown out of the vessel. If it has been previously boiled with solution of potash, and then washed and dried, that portion which is immediately affected by the heat, deflagrates with a report, and scatters the adjacent portions in the undecomposed state. It dissolves sparingly in acids, forming a brown solution. Formic acid does not reduce it. It is insoluble in water. (Berzelius.)

Even when aqueous sesquichloride of osmium and ammonium is mixed with excess of carbonate of potash, the filtrate evaporated to dryness, then saturated with hydrochloric acid, and mixed with potash, a precipitate is obtained which explodes with violent evolution of gas when heated, and therefore still contains ammonia. (Berzelius.)

D. Osmiate of Ammonia.—When ammonia is poured upon osmic acid, the two unite, with evolution of heat, and the compound fuses in yellow drops, which sink to the bottom and solidify in the form of orange-yellow, non-crystalline osmiate of ammonia. This compound when exposed to the air, smells strongly of osmic acid; it dissolves in water, forming a reddish yellow solution, and may be separated therefrom without decomposition, provided no free ammonia has been added to it. (Berzelius.)

¶ E. Osmiamate of Ammonia.—Prepared by decomposing osmiate of silver-oxide with chloride of ammonium. Crystallizes in large crystals, which appear to be isomorphous with those of the potash-salt. They dissolve readily in water and alcohol, and decompose, with explosion, at 125°. (Fritzsche & Struve.) ¶

F. Sulphate of Sesquioxide of Osmium and Ammonia.—Formed by dissolving ammonio-sesquioxide of osmium in dilute sulphuric acid, and evaporating.—Brown, soluble in water.—The excess of sulphuric acid may be removed by evaporation and heating, without reducing the osmium; but the residue, when dissolved in water, leaves a small quantity of basic salt. (Berzelius.)

G. Protochloride of Osmium and Ammonium.—1. When chlorine gas which has been passed over heated osmium, and is consequently mixed with vapour of bichloride of osmium, is received in aqueous ammonia, and the excess of ammonia is expelled from the brown liquid by evaporation, a yellowish brown solution is obtained, apparently containing this salt, and leaving, on evaporation, a brown residue, which, when freed by careful heating from excess of sal-ammoniac, exhibits a greenish hue.—2. When bichloride of osmium and potassium is dissolved in aqueous ammonia, a dark green powder remains, which likewise appears to consist of protochloride of osmium and ammonium. On evaporating the liquid filtered from this powder, and heating the residue till the sal-ammoniac begins to evaporate, protochloride of osmium and ammonium remains, mixed with chloride of potassium. (Berzelius.)

H. Sesquichloride of Osmium and Ammonium.—Formed by dissolving the ammonio-sesquioxide of osmium in strong hydrochloric acid, and evaporating the deep yellowish brown solution to dryness.—Brown-black, amorphous mass, permanent in the air.—When heated in a retort, it fuses imperfectly, swells up (which, however, may be prevented by the addition of a third of its weight of sal-ammoniac), gives off hydrochloric acid, and leaves metallic osmium.—It dissolves in water, forming a brown-black solution, but if it has been too strongly heated, a basic salt remains undissolved in the form of brown flakes. Zinc immersed in the aqueous solution precipitates but a small portion of the osmium, even when heated with excess of acid, and iron none at all. The compound likewise dissolves in alcohol with the same colour, but not so abundantly as in water. (Berzelius.)

I. Terchloride of Osmium and Ammonium.—This composition probably belongs to the salt about to be described. Osmic acid is saturated with aqueous ammonia; the solution left to itself for a few days, at the ordinary temperature of the air, and protected from sunshine; then supersaturated with hydrochloric acid; a small quantity of mercury introduced into the mixture, and frequently shaken up with it for a few days, till the osmic acid has disappeared; and the brownish purple-red liquid evaporated to dryness after the mercury has been poured off. A dark brown residue remains, which is to be dissolved in alcohol; a substance is then left behind, which forms a purple-brown solution in water, and appears to consist of sesquichloride of osmium and ammonium. On the other hand, when the splendid red alcoholic solution is abandoned to spontaneous evaporation, terchloride of osmium and ammonium is left in the form of a brown, confusedly crystalline mass. This substance, when distilled, gives off sal-ammoniac and leaves osmium; it forms an intensely dark red solution in a small quantity of water, and a purple or rose-coloured solution in a larger quantity, like permanganate of potash. Fixed alkalis, in the cold, do not alter the colour of the solution; on digestion, however, a lower degree of oxidation is produced by the action of the ammonia which is set free. (Berzelius.)

K. Nitrate of Sesquioxide of Osmium and Ammonia. — Formed by dissolving the ammonio-sesquioxide in nitric acid. The solution saturated while hot, deposits the compound in the form of a dark brown powder. The acid solution yields, on evaporation, a brown extractive matter, which at 40° dries up to the same brown earthy sub-

stance. This body, when heated in a retort, burns like wet gunpowder and scatters the osmium about in the form of a black, non-metallic powder.—Dissolves sparingly in cold water, much more freely in hot water. (Berzelius.)

When osmiate of potash is distilled with hydrochloric acid, osmic acid is evolved, and there remains a chloride of osmium, from which sal-ammoniac precipitates a minium-coloured salt, very slightly soluble in water, and leaving pure osmium when ignited. (Frémy.)

[It is not yet ascertained which of the chlorides of osmium is contained in this salt.]

## Osmium and Potassium.

A. Protoxide of Osmium with Potash.—When protochloride of osmium and potassium is decomposed with excess of potash, a small quantity of the protoxide remains in the solution, imparting to it a dirty greenish yellow colour. (Berzelius.)

B. Sesquioxide of Osmium with Potash.—Ammonio-sesquioxide of osmium dissolves in aqueous caustic potash and carbonate of potash. (Berzelius.)

C. Teroxide of Osmium with Potash.—*Aqueous.*—Forms a rose-coloured liquid (p. 407 D.). Berzelius.

This composition probably belongs also to the following red salt, which Frémy calls *Osmite of Potash.* Aqueous osmiate of potash mixed with a small quantity of alcohol becomes hot, assumes a red colour, and deposits the salt in the form of a red powder, the osmium indeed being often completely precipitated in this form. The powder is washed with alcohol, which does not dissolve any of it. It crystallizes in beautiful red octohedrons. The weaker acids added to the solution, cause the acid of the red salt to split up into osmic acid and the black oxide. The salt, if immersed in cold aqueous sal-ammoniac, dissolves at first, but afterwards decomposes, depositing a yellow salt, which is scarcely soluble in water, and when ignited in a current of hydrogen gas, leaves pure osmium. (Frémy, *Compt. rend*, 18, 144.)

D. Osmiate of Potash.—1. Formed by mixing osmic acid with aqueous solution of potash, or by saturating hydrate of potash with the vapour of the acid. (Berzelius.)—2. By igniting osmium with hydrate of potash or with nitre; part of the osmic acid, however, is lost by evaporation. (Tennant.)—The solid compound is dark red. (Berzelius.)—The aqueous solution is yellow, and smells slightly of osmic acid. (Tennant); according to Berzelius, on ths contrary, it does not smell at all.

¶ Sulphite of Osmious Oxide and Potash.—Chlorosmiate of potassium is not affected by sulphurous acid at ordinary temperatures; but when a perfectly saturated aqueous solution of sulphurous acid is poured upon the finely pulverized salt, a quantity dissolves, less than that which would be taken up by distilled water. The solution, when heated, undergoes partial decomposition, becoming dark green, in consequence of the separation of black osmic oxide; and if the hot liquid be then filtered, unaltered chlorosmiate of potassium crystallizes out after cooling. But when a solution of the same salt is heated with sulphite of potash, it

acquires first a dark and afterwards a light rose-colour, and at length becomes quite colourless; at the same time, the sulphite of osmious oxide and potash separates out in the form of a white, pulverulent precipitate, which must be collected and well washed.

Light powder, of the texture of magnesia, white, with a tinge of rose-colour, and consisting of small, soft, scaly crystals. It dissolves sparingly in water, and has a scarcely perceptible taste. In other respects it resembles the iridium salt, (p. 384) excepting that it decomposes at 180°, assuming a dingy violet colour, whereas the iridium-salt bears a strong heat without decomposition. (Claus, *Ann. Pharm.* 63, 355.)

| *Anhydrous.* | | | | *Dried at* 100°. | | | Claus. |
|---|---|---|---|---|---|---|---|
| 3KO | 141·6 | .... | 34·65 | 3KO | 141·6 | .... 31·22 | .... 31·14 |
| Os | 99·0 | .... | 24·23 | Os | 99·0 | .... 21·83 | .... 21·90 |
| O | 8·0 | .... | 1·96 | O | 8·0 | .... 1·76 | |
| $5SO^2$ | 160·0 | .... | 39·16 | $5SO^2$ | 160·0 | .... 35·27 | .... 35·20 |
| | | | | 5HO | 45·0 | .... 9·92 | |
| $3(KO,SO^2)+OsO,2SO^2$ | 408·6 | .... | 100·00 | +5Aq. | 453·6 | ....100·00 | |

(Claus, *Ann. Pharm.* 63, 355.) ¶

E. Protochloride of Osmium and Potassium.—*a.* Formed by dissolving protochloride of osmium, together with chloride of potassium, in the smallest possible quantity of water, evaporating, exhausting the residue with a small quantity of water, which leaves behind the greater part of the free chloride of potassium, and again evaporating. Light brown prisms. Alcohol reduces a large quantity of the osmium which they contain. Hence, on attempting to remove the excess of chloride of potassium from the salt by alcohol, the whole of the osmium is reduced in the course of an hour: the portion of the brown crystals not dissolved by the alcohol, forms with water a brown solution, which blackens the skin, and after a while deposits metallic osmium, [reduced by the alcohol still present?].—*b.* By mixing the aqueous solution of bichloride of osmium and potassium with alcohol; filtering from the precipitated salt; distilling the yellow filtrate or exposing it to sunshine, whereupon a small quantity of an ethereal compound is evolved, and a considerable quantity of osmium precipitated; and abandoning the liquid filtered therefrom to spontaneous evaporation.—The salt collects on the sides of the vessel in the form of effloresced, dark green, indistinct crystals, much more soluble in water than in alcohol, and forming a green solution.—(Berzelius.)

F. *Sesquichloride of Osmium and Potassium?*—Doubtful. On mixing a saturated aqueous solution of osmic acid with potash, then with hydrochloric acid, allowing mercury to act upon it till the odour is entirely destroyed, and evaporating the filtrate, a brown double salt is obtained, mixed with free chloride of potassium, and slightly soluble in alcohol. This is perhaps the salt F. (Berzelius.)

G. Bichloride of Osmium and Potassium.—*Chlorosmiate of Potassium.*—Formed by heating an intimate mixture of equal parts of pulverized osmium and chloride of potassium to commencing redness, in a current of chlorine gas. The chlorine is slowly absorbed; to avoid loss of osmium, the unabsorbed portion of the gas is received in ammonia. From the resulting powder, which is black while hot, and of the colour of

minium after cooling, the excess of chloride of potassium is dissolved out by a small quantity of cold water, the residue dissolved in hot water, and the solution left to spontaneous evaporation.

Dark brown, shining, regular octohedrons, yielding a vermillion-coloured powder. The salt withstands gentle ignition, gives off chlorine gas together with a small quantity of sublimed protochloride of osmium, and leaves chloride of potassium, mixed with white, metallic-looking osmium. When distilled with nitric acid, it yields osmic acid, and leaves nitre, together with chloride of potassium. Dissolves in cold water with a lemon-yellow colour, and more abundantly in hot water, with a deep yellow colour, inclining to green. Paper moistened with the aqueous solution, and exposed to sunshine, acquires a blue colour, which cannot be removed by washing. The aqueous solution is not affected by sulphurous acid, even at a boiling heat; alcohol precipitates the dissolved substance in the form of a vermillion-coloured, crystalline, powder, the liquid retaining its yellow colour. (Berzelius.)

The compounds of osmium have, as shown by Berzelius, a disposition to unite with those of iridium. Hence, when native osmide of iridium mixed with chloride of potassium is heated to redness in chlorine gas, a mixture of chlorosmiate and chloriridiate of potassium is obtained, in brown-black octohedrons. The analysis of this salt is given in the following table; its formula is $2(KCl,IrCl^2)+KCl,OsCl^2$.—This salt, mixed with an equal weight of carbonate of soda, and ignited, gives off the greater part of the osmium in the form of osmic acid, and leaves sesquioxide of iridium, still containing a little osmic oxide, which may be removed by digesting in aqua-regia, then reducing the iridium, and heating it to redness in the air. (Hermann, *Pogg.* 37, 407.)

| | | | Berzelius. |
|---|---|---|---|
| KCl | 74·6 | 30·52 | 30·46 |
| Os | 99·0 | 40·51 | 40·64 |
| 2Cl | 70·8 | 28·97 | 28·90 |
| $KCl,OsCl^2$ | 244·4 | 100·00 | 100·00 |

| | | | Hermann. |
|---|---|---|---|
| 2KCl | 223·8 | 30·53 | |
| Os | 99·0 | 13·50 | 13·4 |
| 2Ir | 198·0 | 27·00 | 26·6 |
| 6Cl | 212·4 | 28·97 | |
| $2(KCl,IrCl^2)+KCl,OsCl^2$ | 733·2 | 100·00 | |

¶ Bisulphite of Osmious Oxide with Chloride of Potassium. —$3KCl+OsO,2SO^2$.—Formed by treating the salt E with hydrochloric acid.—Brown-red, crystalline salt, very soluble, and having a sharp taste. Anhydrous.—(Claus, *Ann. Pharm.* 67, 375.)

| | | | Claus. |
|---|---|---|---|
| 3K | 117·6 | 29·76 | 29·38 |
| Os | 99·0 | 25·06 | 25·00 |
| O | 8·0 | 2·17 | 2·47 |
| $2SO^2$ | 64·0 | 16·16 | 16·40 |
| 3Cl | 106·2 | 26·85 | 26·75 |
| | 394·8 | 100·00 | 100·00 |

¶ H. Osmiamate of Potash.—Prepared in the manner already described (p. 413), or better, by dissolving solid osmic acid in a strong solution of potash mixed with ammonia, and agitating the mixture.

The liquid then assumes a light yellow colour, and finally deposits the salt in the form of a yellow granular powder. The salt may likewise be produced by passing the vapours of the distilled osmic liquors (obtained in the treatment of platinum ore) into ammoniacal potash-ley properly cooled: care must, however, be taken to avoid the simultaneous distillation of nitrous vapours, which would exert a decomposing action on the osmiamate. Carbonate of potash may be substituted for caustic potash; but it is less advantageous. To obtain the salt in definite crystals, the powder first obtained must be dissolved in the smallest possible quantity of boiling water, and the solution left to cool; the salt is then deposited in small, lemon-yellow crystals. Larger crystals may be obtained by forming a saturated solution in the cold, and leaving it to spontaneous evaporation; they then take the form of acute, square-based octohedrons. The crystals are anhydrous. The salt is much less soluble in alcohol than in water; it dissolves, however, in the former without alteration, and suffers but slight decomposition during the evaporation of the solution. It is insoluble in ether. (Fritzsche & Struve.)

| | *Calculation*, according to Fritzsche & Struve. | | | Fritzsche & Struve.[3] | *Calculation*, according to Gerhardt. | | |
|---|---|---|---|---|---|---|---|
| KO | 47·2 | .... | 16·14 | .... 16·13 | KO | 47·2 | .... 15·77 |
| 2Os | 198·0 | .... | 68·10 | .... 67·90 | 2Os | 198·0 | .... 66·17 |
| N | 14·0 | .... | 4·80 | .... 4·82 | N | 14·0 | .... 4·68 |
| 4O | 32·0 | .... | 10·96 | .... 11·15 | 5O | 40·0 | .... 13·38 |
| $KO,Os^2NO^4$ | 291·2 | .... | 100·00 | .... 100·00 | $KO,Os^2NO^5$ | 299·2 | ....100·00 |

When this salt is moistened with strong hydrochloric acid, a strong action is immediately set up, accompanied by a disengagement of chlorine, or perhaps of an oxide of chlorine; the acid acquires a fine purple-red colour; and the crystals of the salt become covered with a crust consisting of two kinds of crystals, into which the original crystals are in the end completely converted. Hydrochloric acid added to a cold saturated solution of osmiamate of potash, does not decompose it at ordinary temperatures; but, on the application of heat, the liquid acquires a transient red colour, then turns brown, and gives off osmic acid. If the boiling be continued till this last effect ceases, and the liquid evaporated to the crystallizing point, three salts are deposited, viz., a green salt in the form of hexagonal tables, another green salt in needles, and a red salt, all of which appear to decompose as they dissolve in water; they have not been further investigated. (Fritzsche & Struve.)

### Osmium and Sodium.

Osmiamate of Soda.—More soluble than the potash-salt, and therefore best prepared by decomposing the silver-salt with chloride of sodium. The solution, when evaporated, yields syrupy crystals at first, but afterwards prismatic crystals are formed. (Fritzsche & Struve.)

### Osmium and Barium.

Osmiamate of Baryta.—Prepared by decomposing the silver-salt with chloride of barium. Crystallizes readily in yellow shining needles; tolerably soluble in water; detonates at 150°. (Fritzsche & Struve.)

| | *Calculation*, according to Fritzsche & Struve. | | Fritzsche & Struve. | *Calculation*, according to Gerhardt. | | |
|---|---|---|---|---|---|---|
| BaO | 76·7 | 23·79 | 23·88 | BaO | 76·7 | 23·33 |
| 2Os | 198·0 | 61·89 | 61·07 | 2Os | 198·0 | 60·24 |
| N | 14·0 | 4·36 | 4·27 | N | 14·0 | 4·25 |
| 4O | 32·0 | 9·96 | 10·78 | $O^5$ | 40·0 | 12·18 |
| $BaO,Os^2NO^4$ | 320·7 | 100·00 | 100·00 | $BaO,Os^2NO^5$ | 328·7 | 100·00 |

¶

## Osmium and Calcium.

Osmiate of Lime.—Aqueous osmic acid forms with lime, a light yellow liquid, which yields a dark red precipitate with infusion of galls. (Tennant.) A small quantity of formic acid added to the solution, throws down blue metallic osmium. (Fr. Weiss & Döbereiner, *Ann. Pharm.* 14, 17.)—Vapours of osmic acid passed into excess of lime-water produce yellow flakes (p. 259, No. 26). (Vauquelin.)

## ¶ Osmium and Zinc.

Osmiamate of Zinc-oxide.—Easily soluble; not obtained in the solid state. (Fritzsche & Struve.)

B. Ammonio-osmiamate of Zinc-oxide.—1. Formed by adding a zinc-salt to a solution of osmic acid in ammonia.—2. By mixing the potash-salt with ammonia, and then adding a zinc-salt.—Light yellow, crystalline powder, which may be dried in the air without loss; is insoluble in ammonia; is decomposed by water, even in the cold, and completely on boiling, the whole of the zinc-oxide separating out, and osmiamate of ammonia remaining in solution. (Fritzsche & Struve.)

| | *Calculation*, according to Fritzsche & Struve. | | Fritzsche & Struve. | *Calculation*, according to Gerhardt. | | |
|---|---|---|---|---|---|---|
| $2NH^3$ | 34·0 | 10·69 | 10·35 | $2NH^3$ | 34·0 | 10·41 |
| ZnO | 40·2 | 12·63 | 12·28 | ZnO | 40·2 | 12·33 |
| $Os^2NO^4$ | 244·0 | 76·68 | | $Os^2NO^5$ | 252·0 | 77·26 |
| $2NH^3,ZNO,Os^2NO^4$ | 318·2 | 100·00 | | $2NH^3,ZnO,Os^2NO^5$ | 326·2 | 100·00 |

[Gerhardt's formula for this salt agrees more closely with the analytical results than that of Fritzsche & Struve.] ¶

## Osmium and Tin.

*Osmiate of Tin?*—Osmiate of lime forms a brown precipitate with protochloride of tin. (Tennant.)

## Osmium and Lead.

A. Osmiate of Lead-oxide.—Osmiate of lime yields a yellowish brown precipitate with lead-salts. (Tennant.)

¶ B. Osmiamate of Lead-oxide.—Nitrate of lead-oxide forms no immediate precipitate with osmiamate of potash, but after some time

crystals are formed, which decompose with facility.—A solution of acetate of lead-oxide forms with solutions of the osmiamates, a non-crystalline precipitate, which at first exhibits a dirty yellow colour, but soon acquires a purple tint, and gives off osmic acid. (Fritzsche & Struve.)

C. Chlorosmiamate of Lead.—$PbCl, PbO, Os^2NO^4$?—When a solution of chloride of lead, or of the nitrate mixed with hydrochloric acid is added to a solution of osmiamate of potash, a yellow crystalline precipitate is gradually formed, which appears to have the composition just given. (Fritzsche & Struve.) ¶

## Osmium and Copper.

Osmide of Copper.—Very malleable; easily soluble in aqua-regia; the solution gives off osmic acid when distilled. (Tennant.)

## Osmium and Mercury.

A. Osmium-amalgam.—Aqueous osmic acid decomposed by mercury, yields a soft amalgam, which becomes more compact when the excess of mercury is removed by pressure. On distilling this amalgam, metallic osmium remains in the form of powder. (Tennant.)

B. Osmiate of Mercury.—Osmiate of lime forms a white precipitate in solutions of mercury. (Tennant.)

C. Protochloride of Osmium and Mercury.—When osmic acid, dissolved in aqueous hydrochloric acid, is left in contact with mercury, reduction is set up, but ceases after a while; and the brownish liquid deposits, on evaporation, a transparent, shining, purple-red, amorphous salt, having a metallic taste. Iron or zinc immersed in its aqueous solution, precipitates nothing but mercury, while protochloride of osmium, and iron, or protochloride of osmium and zinc, remains in solution. (Berzelius.)

¶ D. Osmiamate of Mercurous Oxide.—Light yellow precipitate; amorphous, and insoluble in water; does not explode when heated. (Fritzsche & Struve.)

E. Osmiamate of Mercuric Oxide.—Prismatic crystals, which decompose very quickly. (Fritzsche & Struve.)

## Osmium and Silver.

Osmiamate of Silver-oxide.—1. Formed by dissolving osmic acid in an ammoniacal solution of a silver-salt, and then supersaturating with nitric acid.—2. By adding a silver-salt to an ammoniacal solution of osmic acid, previously mixed with excess of nitric acid.—3. By adding a silver-salt to a soluble osmiamate. Lemon-yellow, crystalline powder, very slightly soluble in water and in cold nitric acid; more soluble in ammonia, with which also it is capable of combining. When protected

from light, it may be dried in vacuo, over sulphuric acid, without blackening; ultimately, however, it decomposes, and gives off osmic acid. At 80°, it decomposes suddenly, and with violent detonation; percussion causes it to undergo a similar decomposition. A violent detonation is likewise observed when sulphuretted hydrogen is passed over the dried salt. Hot nitric acid readily decomposes the salt; the liquid first acquires a brown colour, then gradually becomes colourless, and gives off osmic acid. (Fritzsche & Struve.)

| *Calculation*, according to Fritzsche & Struve. | | | Fritzsche & Struve. | *Calculation*, according to Gerhardt. | | |
|---|---|---|---|---|---|---|
| AgO | 116 | 32·15 | 32·09 | AgO | 116 | 31·52 |
| 2Os | 198 | 55·10 | 55·01 | 2Os | 198 | 53·82 |
| N | 14 | 3·88 | | N | 14 | 3·81 |
| 4O | 32 | 8·87 | | 5O | 40 | 10·85 |
| | 360 | 100·00 | | $AgO,Os^2NO^5$ | 368 | 100·00¶ |

## Osmium and Gold.

Osmide of Gold.—Very malleable alloy, which behaves with aqua-regia, just like osmide of copper. (Tennant.)

## Osmium and Iridium.

A. Osmide of Iridium.—Found native (p. 254).—According to Berzelius, it consists partly of IrOs, partly of $IrOs^3$, partly of $IrOs^4$.—But whatever may be its proportional composition, specific gravity, and behaviour in the alcohol flame, the crystalline form remains the same; namely, that of *Fig.* 135 and 137. The prisms are very much shortened: $r : p = 118°$; $r : s = 152°$. Cleavage parallel to $p$. According to this, iridium and osmium must be isomorphous. (G. Rose, *Pogg.* 29, 452; 54, 537.) This form has been previously described by Bournon.

Osmide of iridium is extremely hard and brittle, has a specific gravity of 16·4—16·21, the colour of platinum, and generally a strong lustre. When heated in the air, it gives off osmic acid, with greater facility in proportion as it is richer in osmium, and becomes dull. When ignited for some time with nitre, or with hydrate of potash and nitre, it gives off part of its osmic acid, and forms osmiate of potash and the compound of sesquioxide of iridium with potash. According to Fischer (*Pogg.* 18, 258), it is decomposed much more easily by nitrate of lime, the decomposition taking place, indeed, even at a low red heat. Aqua-regia has scarcely any action upon osmide of iridium. To expel the osmium from a specimen of osmide of iridium, and determine the amount of iridium, the mineral is ignited in a crucible, and a drop of oil of turpentine let fall on it from time to time by means of a platinum wire with a loop at the end, the crucible being covered after each addition of the turpentine, and then opened again from time to time. The oil reduces the oxidized metals with evolution of light and heat; and on opening the crucible, the charcoal burns and oxidizes together with the osmium, which, by frequent repetition of the process, may be completely expelled. This process, however, is applicable only to $IrOs^4$ and $IrOs^3$, not to IrOs. (Berzelius.)

¶ Fritzsche and Struve decompose osmide of iridium by adding

3 parts of the mineral in its natural state (not pulverized,) to a mixture of 1 pt. hydrate of potash and 1 pt. chlorate of potash, fused in a capacious iron crucible over a spirit-lamp. The action commences as soon as the chlorate of potash begins to give off its oxygen, the mixture acquiring a yellowish brown colour, and frothing up so violently that it is necessary to reduce the heat. The fused mass then becomes very viscid, giving off large bubbles of oxygen, and the osmide of iridium, which at first remains at the bottom, is then diffused throughout the whole mass, whereby the action is greatly facilitated. When this stage of the operation is attained, the action goes on without any further application of heat from without, and after a while, the mixture becomes nearly black and solid. Up to this point no fumes of osmic acid are evolved, but as the mass solidifies, that compound is given off in small quantity, especially if the application of heat be continued. On treating the cooled mass with water, an orange-yellow solution is formed, containing osmium and ruthenium, and a bluish black precipitate containing iridium, easily separated from the undecomposed osmide of iridium. This is the most convenient of all methods of decomposing osmide of iridium, because it is almost entirely free from the annoyance and danger attending the evolution of osmic acid. The only inconvenience attending is, that the crucibles are always attacked; platinum crucibles are attacked by the caustic potash; if a silver vessel be used, chloride of silver is formed, and mixes with the product; gold crucibles would be the best, if they were not too costly. On the whole, the process is best performed in iron crucibles, but the product is then always more or less contaminated with oxide of iron. (*J. pr. Chem.* 37, 483; H. Rose's *Analyt. Chem.* II. 241). ¶

The crystals examined by G. Rose were as follows:

*a.* From Newiansk. Of specific gravity 19·386, and the hardness of quartz; tin-white; does not alter or emit any odour of osmium when heated upon charcoal before the blowpipe; when fused with nitre, it smells faintly of osmium; does not dissolve in fused microcosmic salt or in aqua-regia.

*b.* From Nischne Tagil. Of specific gravity 21·118, and of the hardness of quartz; lead-grey; when heated upon charcoal before the blowpipe, it loses its lustre, blackens slightly, and diffuses a penetrating odour of osmium; when held by a pair of platinum forceps in an alcohol flame, it renders the flame luminous, and colours it yellowish red.

Berzelius (*Pogg.* 32, 232) distinguishes the following varieties of osmide of iridium:

*a. Brazilian.* Small, irregular grains, which look as if they were corroded, and are sometimes flat, smooth, white, and shining, with a specific gravity of 16·445 (or 19·5, according to Wollaston).

*b. Siberian.* Often constitutes the principal part of platinum-ore, especially of that from Katharinenburg, Slatoust, and Kischtin.—*α.* Resembles the Brazilian; sp. gr. from 18·645 to 19·25.—*β.* The most common variety. Its composition is about IrOs. Flat, smooth, shining laminæ, which scratch glass, and make an impression upon a steel plate, when broken upon it; sp. gr. 19·25. When ignited in a platinum spoon, they produce only a momentary luminosity in the alcohol flame (p. 409). —*γ.* Crystallized; partly $IrOs^3$, partly $IrOs^4$, intermixed in separate granules. When heated to redness in a platinum spoon, it gives off a very large quantity of osmic acid, acquiring, in consequence, a burnt aspect and a darker colour. These grains, consisting of $IrOs^4$, decompose, when heated in the air, much more quickly than those which consist

of $IrOs^3$, although they previously exhibit no difference in aspect or in colour.—Since, according to Gustav. Rose, the crystals which are richer in osmium have the specific gravity 21·118, and consequently the osmide of iridium is specifically heavier in proportion as it contains more osmium, it would appear that osmium in the compact state is denser than iridium. So far Berzelius.

| | Berzelius. | | | | Thomson. |
|---|---|---|---|---|---|
| | | Katharinenburg. | | | America. |
| | *b*, *β*. | *γ. Crystallized.* | | *γ. Crystallized.* | |
| Pd..... | trace | | | | |
| R ..... | 3·15 | | | | |
| Ir ..... | 46·77 | | | | |
| Os..... | 49·34 | ..... 25·1 | .... | 20 ..... | 75·00 |
| Fe..... | 0·74 | ..... | .... | ..... | 25·10 |
| | | | | | 2·77 |
| | 100·00 | ..... | | | 102·87 |

Many varieties of osmide of iridium contain small quantities of gold. (Wöhler.)

According to Tennant, osmide of iridium may be fused with bismuth, zinc, tin, lead, copper, silver, and gold.—No definite compound is thereby produced, but the grains of osmide of iridium are merely enveloped by the other metal, and remain unaltered, when that metal is dissolved in acids. (Berzelius.)—Wöhler (*Ann. Pharm.* 39, 336) found osmide of iridium in gold which had been worked.—According to Faraday and Stodart (*Ann. Chim. Phys.* 21, 73), 1 part of osmide of iridium forms with 33·3 parts of iron, a bluish mixture, which, though it contains no carbon, may be hardened to a certain extent like steel, and rusts much less quickly than that substance.—Osmide of iridium appears capable of uniting by fusion with steel in all proportions.

B. Compound of the Sesquioxides of Iron and Chromium with the Protoxides of Iridium and Osmium.—*Irite.*—Found in the native platinum of the Ural, often filling up the interstices between the separate grains in large masses of platina.—Remains behind, when platina of this description is digested in aqua-regia, mixed with titaniferous iron, chrome-iron ore, and hyacinths, and, in consequence of its greater levity, may be separated from these minerals by levigation. Soft, strongly lustrous, black, graphitic scales, having a density of 6·056, and attracted by the magnet. Completely decomposed when mixed with chloride of potassium and ignited in a current of chlorine gas, whereby a dark brown powder is obtained, perfectly soluble in water, and forming a red solution. This solution, when diluted, deposits reddish-black octohedrons of chlorosmiate of potassium and sesquichloride of chromium. By fusion with nitre, it is oxidized with evolution of osmic acid. It does not dissolve in any acid. (Hermann, *J. pr. Chem.* 23, 276.)

| | *Approximate Calculation.* | | | Hermann. | | |
|---|---|---|---|---|---|---|
| | | | | *a.* | | *b.* |
| 10IrO..... | 1070 | .... | 60·66 ..... | 60·60 | $Ir^2O^3$.... | 62·86 |
| 2OsO..... | 214 | .... | 12·13 ..... | 10·30 | | 10·30 |
| $3Fe^2O^3$ ..... | 240 | .... | 13·60 ..... | 13·89 | FeO .... | 12·50 |
| $3Cr^2O^3$ ..... | 240 | .... | 13·61 ..... | 13·70 | | 13·70 |
| $Mn^2O^3$..... | | .... | ..... | trace | | trace |
| | 1764 | .... | 100·00 ..... | 98·49 | | 99·36 |

*b* is Hermann's analysis as given by himself; in *a*, the sesquioxide of iridium assumed to exist in the mineral by Hermann, is reckoned as protoxide, and his protoxide of iron as sesquioxide, to make the analysis accord with the preceding formula. According to this, the formula should be $2(IrO; OsO), (Fe^2O^3; Cr^2O^3)$, or more exactly: $2IrO, Fe^2O^3 + 2(\frac{2}{3}IrO, \frac{1}{3}OsO)\ Cr^2O^3$. This supposed constitution, however, is irreconcilable with the magnetism of the irite, unless that property be due to the admixed chrome-iron ore.—The formula given by Hermann is: $OsO, 3Ir^2O^3 + 4FeO, 3Cr^2O^3$; that of Berzelius (*Jahresber.* 22, 191) is: $FeO, 3Ir^2O^3 + FeO, OsO^2 + 3(FeO, Cr^2O^3)$.

# ADDENDA.

To page 86.—*Action of Acids and Acid Salts on Infusible White Precipitate.*—1. When this compound is boiled with water mixed with a sufficient quantity of acid to dissolve it, the solution yields on evaporation white laminar crystals, having the composition,—

$$2(HgO,SO^3) + NH^4Cl + HgCl;$$

and the mother-liquor contains sulphate of ammonia and sulphate of mercuric oxide. Ether dissolves out protochloride of mercury from the crystals; water colours them yellow, and forms a basic salt.

2. Water strongly acidulated with nitric acid, acts but slightly upon white precipitate in the cold, but dissolves it when heated. The solution, when evaporated, first yields an abundance of white, laminar, silvery crystals, having the composition,—

$$4HgCl + NH^4O,NO^5;$$

they are insoluble in water, and, when digested in ether, give up to that liquid a large quantity of protochloride of mercury; on further evaporation, the mother-liquor yields small, metallic-looking, oblique prisms, which appear to be a mixture of protochloride of mercury with a large quantity of nitrate of mercuric oxide and ammonia.

3. Equal parts of white precipitate, chloride of ammonium, and hydrochloric acid, heated with 15 parts of water, form a solution, which, on evaporation, first yields crystals of chloride of sodium, and afterwards metallic-looking, four-sided laminæ, soluble in water, and consisting of,—

$$4HgCl + NH^4Cl + 4NaCl.$$

4. White precipitate boiled with twice its weight of binoxalate of potash, and a sufficient quantity of water, leaves an insoluble residue of mercurous oxalate, the decomposition being attended with evolution of carbonic acid; the solution, when exposed to the direct rays of the sun, yields a precipitate of calomel.

5. White precipitate boiled with three times its weight of cream of tartar, and a sufficient quantity of water, liberates carbonic acid, and forms a solution, which, when evaporated, yields a succession of crystalline salts, differing from one another in appearance, and not yet satisfactorily examined.

6. White precipitate boiled with acetic acid, also gives rise to evolution of carbonic acid and precipitation of calomel. The solution, when evaporated, yields yellow crystalline crusts, which soon blacken on exposure to light, and contain 72·9 per cent. of mercury and 13·0 chlorine; they appear to be a *sexbasic acetate* of *mercuric amido-chloride* + 12 *At. water.*

7. White precipitate forms, with sulphate of quinine and very dilute sulphuric acid, a solution yielding indistinct crystals, which, after recrystallization from alcohol, appear to be composed of,

$$12SO^3 + 6 \text{ quinine} + 2SO^3 + HgO,NH^4O + HgCl.$$

(Kosmann, *N. J. Pharm.* 14, 321; *J. pr. Chem.* 46, 81; abstr. *Jahresbericht*, L & K, 1847—8, 448.)

To page 142.—*Precipitation of Silver in the Metallic State.*—For separating silver in the metallic state from its solution (containing lead or copper), Kessler recommends the use of acetate of ferrous oxide, which precipitates the silver completely, whereas green vitriol does not. The solution must be as free as possible from excess of acid, and largely diluted with water. (*N. J. Pharm.* 11, 86; *Jahresb.* 1847—8, 449.)—According to Mohr (*Ann. Pharm.* 66, 65), when a pure silver-solution is treated in the cold with ferrous acetate, a dazzling white precipitate of silver-acetate is first formed, but is quickly converted into metallic silver, the reduction beginning in isolated black points, and rapidly spreading throughout the whole mass. From solutions containing copper and free nitric acid, metallic silver separates at once.

To pp. 135 and 165.—*Reduction of Chloride of Silver.*—According to Mohr (*Ann. Pharm.* 66, 65), the best of all reagents for this purpose is metallic zinc. With regard to Gregory's method of converting the chloride of silver into oxide, by boiling with strong potash-ley, Mohr observes, that part of the chloride of silver is apt to cake together, and thereby escape decomposition, and that the process succeeds best when the chloride of silver is previously levigated with water, and added to the potash-solution at a boiling heat. With respect to Levol's method of boiling chloride of silver with potash-ley and sugar, Mohr finds that complete decomposition is thereby obtained, and that the reduced silver cakes together in dense masses, from which the liquid is easily decanted.

To page 165.—*Decomposition of Chloride of Silver by Metallic Sulphides and Arsenides.*—According to Malaguti and Durocher (*Compt. rend.* 25, 160), many metallic sulphides and arsenides have the power of decomposing chloride of silver, with comparative quickness when that compound is in the state of solution, more slowly by mere contact.

| | | | | | | |
|---|---|---|---|---|---|---|
| 100 | parts | ZnS | decompose | 3 | parts | AgCl. |
| 100 | — | CdS | —— | 14 | ——— | |
| 100 | — | $BiS^3$ | —— | 2 | ——— | |
| 100 | — | PbS | —— | 5 | ——— | |
| 100 | — | SnS | —— | $\frac{1}{2}$ | ——— | |
| 100 | — | $SnS^2$ | —— | 30 | ——— | |
| 100 | — | $Cu^2S$ | —— | 360 | ——— | |
| 100 | — | $SbAs^3$ | —— | 120 | ——— | ? |

and 100 parts of arsenide of cobalt decompose 166 chloride of silver. The same compounds in the form of minerals, from various localities, frequently exhibited very different degrees of decomposing power. Bromide of silver was decomposed to a certain extent by the same compounds; iodide of silver, not at all.

To page 166.—*Solubility of Chloride of Silver in Hydrochloric Acid.*—According to Pierre (*N. J. Pharm.* 12, 237), 1 part of chloride of silver dissolves in 200 parts of strong hydrochloric acid, and in 600 parts of the same acid diluted with twice its weight of water.

END OF VOL. VI.

# REPORT

OF

# THE FOURTH ANNIVERSARY MEETING

OF THE

# CAVENDISH SOCIETY.

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The Anniversary Meeting of the Cavendish Society for the year 1851 was held at No. 19, Montague Street, Russell Square, on Saturday, the 1st of March, at three o'clock in the afternoon.

The Chair was taken by Thomas Graham, Esq., F.R.S., President, who called upon the Secretary to read

## THE REPORT OF THE COUNCIL.

"In their last Annual Report the Council referred with satisfaction to the progressive advancement of the Society, as indicated by the increasing number of its Members; and they expressed a hope that a similar extension would be effected during the year which then commenced. Such an extension seemed to be required in order to place the Society upon a safe and permanent basis, and to insure the complete realization of its objects. Considering the greatly increased extent to which the science of Chemistry has been cultivated in this country within the last few years, as compared with former times, it was thought that a considerable accession of Members might be obtained, and it was confidently anticipated, as the published works of the Society became better known, that the advantages resulting from such an Association would be more amply and adequately appreciated.

"The Council, on reviewing the results of the past year's operations, see no cause for discouragement, although they must admit that all that they desired has not been fully attained. The number of Members has undergone a slow but constantly occurring augmentation, and if the aggregate number be still not so great as it is desirable it should be, there is, nevertheless, every reason to believe that the limit to further extension has not been reached.

"A reference to the financial statements of former years will show the annual progress which has been made by the Society. Thus, in March 1849, 556 Members had paid the subscription for the year 1848, and there were besides about 100 from whom the subscription had not been received, making the number of Members 656. In March 1850, the number of Subscribers for 1848 had been augmented to 791, some of whom, however, had previously retired; and the numbers for 1849 were 694 who had paid, and 56 whose subscriptions were due, making the number of Members at that time 750. During the past year, an increase has been effected to about the same extent as that which occurred in the preceding year, the Subscribers for 1848 having been augmented to 885, and those for 1849 to 854. This last number may be considered to represent the extent of the Society at the present time.

"The Members have received the fourth and fifth volumes of Gmelin's 'Handbook of Chemistry' for the past year, and the Council have pleasure in announcing that Dr. Wilson's work on Cavendish is now ready, and will be immediately distributed to the Subscribers of 1849. It was thought desirable to proceed with as little delay as possible in bringing out the former of these works, of which there remains but one more volume to complete the Inorganic part, and this the Members will receive in the course of the present year. The delay that has attended the publication of the 'Life of Cavendish,' although unavoidable, was regretted by the Council, but they believe it has been more than compensated for by the large amount of interesting matter which the author was enabled to collect whilst seeking for some of the details of the biography without which he was unwilling to send his work before the public. The characteristic portrait of Cavendish, which forms the frontispiece to the book, has been obtained through the instrumentality of a Member of the Society, Mr. Tomlinson. It is

copied from a drawing, by Alexander, in the print-room of the British Museum, and is considered, by those who knew the philosopher, to be a good and striking likeness. These accessions of matter have not only enhanced the value of the work as a literary production, they have also added to the expenses of publication,—a result which makes it necessary to limit the works issued for 1850 to the two volumes of Gmelin's Chemistry, now in the hands of Members.

"There are several works in course of preparation, to be published in this or succeeding years.

"The first volume of the translation of Lehmann's Physiological Chemistry, by Dr. Day, is now in the hands of the printer, and this will be the first of the books to be issued for 1851. It will be followed by the sixth volume of Gmelin's Chemistry, which will conclude the Inorganic part of this work. The Organic part will then be immediately proceeded with.

"The translation of the Essays of Saussure is prepared, and the abstracts of the works of Hales, Ingenhousz, Sennebier, Wiegmann, and other contemporaneous writers on the chemistry of vegetation, are nearly completed.

"Some of the Members have expressed a desire that the translation of Bischof's Elements of Chemical and Physical Geology, which is among the works proposed for publication by the Society, should be commenced at an early period, but the Council have not hitherto found it practicable to make arrangements to this effect without retarding the completion of books previously undertaken.

"It has been suggested to the Council, that a valuable work, for the use of practical chemists, might be prepared through the co-operation of the Members of this Society. Most men engaged in scientific investigations, have occasion to refer to tables for facilitating the calculation of results; yet there is no work extant in which there is a good and complete collection of such as relate to all the different departments of applied chemistry. It is proposed that the publication of a work, to be entitled 'Chemical formulæ, and constants, for use in the Laboratory,' be undertaken by the Society; and should this proposition be favourably received

by the Members, and a prospect afforded of the means of obtaining the required matter, the Council will be prepared to carry it into effect.*

"The first of the Society's publications, the volume of Chemical Reports and Memoirs, edited by Professor Graham, being out of print, those who now join the Society, and desire to obtain the whole of Gmelin's Chemistry, are supplied with the first volume on payment of half the subscription for 1848. In anticipation of a continued demand, by new members of the Society, for all the volumes of Gmelin's standard work, a larger number was printed than was immediately required, and copies still remain on hand.

"The Council trust that the interest evinced in the objects of the Association has been justified by the results of its operations, and that the exertions made for extending the limits of the Society, will not be relaxed until it has reached the point originally contemplated, and which is now so nearly approached."

* The Council will be glad to receive communications on this subject addressed to the Secretary, from members who may be able to afford assistance by supplying or suggesting matter for the proposed work.

# Treasurer's Statement of the Receipts and Expenditure of the Cavendish Society, from the 1st of March, 1850, to the 27th of February, 1851.

## Receipts.

| | | | £ | s. | d. |
|---|---|---|---|---|---|
| Balance from previous year | | | 278 | 18 | 6 |
| 94 | Subscriptions for | 1848 | 85 | 11 | 6 |
| 160 | Ditto | 1849 | 168 | 0 | 0 |
| 684 | Ditto | 1850 | 718 | 4 | 0 |
| 95 | Ditto | 1851 | 99 | 15 | 0 |
| 1 | Ditto | 1852 | 1 | 1 | 0 |
| | | | £1351 | 10 | 0 |

## Expenditure.

| | £ | s. | d. |
|---|---|---|---|
| Stationery, Postage, and Petty cash | 15 | 4 | 3 |
| Advertisements | 5 | 9 | 0 |
| Insurance | 2 | 6 | 6 |
| Collector's Commission | 12 | 11 | 3 |
| Secretary | 75 | 0 | 0 |
| Editorial expenses | 195 | 15 | 0 |
| Paper | 145 | 16 | 7 |
| Printing | 395 | 2 | 0 |
| Engraver | 2 | 11 | 0 |
| Binding and wrapping | 94 | 10 | 6 |
| | 944 | 6 | 1 |
| Balance in hand | 407 | 3 | 11 |
| | £1351 | 10 | 0 |

We have examined the above statement, and find it correct.

R. PORRETT.

Feb. 28, 1851. R. H. SEMPLE.

It was moved by Mr. Porrett, seconded by Mr. Button, and resolved,

"That the Report just read be received and adopted."

The Meeting then proceeded to the election of Officers for the ensuing year, and the following were declared to have been duly elected;

### President.

Professor Graham, F.R.S.

### Vice-Presidents.

Arthur Aikin, F.G.S.
Professor Brande, F.R.S.
Earl of Burlington, F.R.S.
Sir James Clark, M.D., F.R.S.
Professor T. Clark, M.D.
Walter Crum, F.R.S.
Michael Faraday, D.C.L., F.R.S.
J. P. Gassiot, F.R.S.
Sir. R. K. Kane, M.D., F.R.S.
W. A. Miller, M.D.,F.R.S.
Richard Phillips, F.R.S.
Professor Wheatstone, F.R.S.

### Council.

Jacob Bell, M.P., F.L.S.
Golding Bird, M.D., F.R.S.
Warren de la Rue, F.R.S.
W. Ferguson, F.C.S.
J. J. Griffin, F.C.S.
A. W. Hofmann, Ph.D., F.R.S.
G. D. Longstaff, M.D., F.C.S.
T. N. R. Morson, F.L.S.
Jonathan Pereira, M.D., F.R.S.
R. Porrett, F.R.S.
R. H. Semple, M.D.
W. Sharpey, M.D., F.R.S.
Alfred S. Taylor, M.D., F.R.S.
Charles Tomlinson, Esq.
Robert Warington, F.C.S.
A. W. Williamson, Ph.D., F.C.S.

### Treasurer.

Henry Beaumont Leeson, M.D., F.R.S., St. Thomas's Hospital.

### Secretary.

Theophilus Redwood, Esq., 19, Montague Street, Russell Square.

It was moved by Dr. Semple, seconded by Mr. T. Hubbuck, and resolved,

"That Dr. Basham, J. E. Bowman, Esq., and Percival Johnson, Esq., be appointed Auditors for the ensuing year,"

The following Resolutions were then proposed and unanimously adopted:—

Moved by Mr. BUTTON, seconded by Mr. MAITLAND,

"That the thanks of the Meeting be given to the PRESIDENT, TREASURER, and COUNCIL, for their services to the Society."

Moved by Mr. WARREN DE LA RUE, seconded by Mr. JACOB BELL,

"That the thanks of the Meeting be given to the HONORARY LOCAL SECRETARIES for their services to the Society."

The Meeting was then adjourned.

THEOPHILUS REDWOOD, SECRETARY,
19, Montague Street, Russell Square.

MARCH 1ST, 1851.

# CAVENDISH SOCIETY.


## President.

Professor Graham, F.R.S.

## Vice-Presidents.

Arthur Aikin, F.G.S.
Professor Brande, F.R.S.
Earl of Burlington, F.R.S.
Sir James Clark, M.D., F.R.S.
Professor T. Clark, M.D.
Walter Crum, F.R.S.
Michael Faraday, D.C.L., F.R.S.
J. P. Gassiot, F.R.S.
Sir R. Kane, M.D., F.R.S.
W. A. Miller, M.D., F.R.S.
Richard Phillips, F.R.S.
Professor Wheatstone, F.R.S.

## Council.

Jacob Bell, M.P., F.L.S.
Golding Bird, M.D., F.R.S.
Warren de la Rue, F.R.S.
W. Ferguson, F.C.S.
J. J. Griffin, F.C.S.
A. W. Hofmann, Ph.D., F.R.S.
G. D. Longstaff, M.D., F.C.S.
T. N. R. Morson, F.L.S.
Jonathan Pereira, M.D., F.R.S.
R. Porrett, F.R.S.
R. H. Semple, M.D.
W. Sharpey, M.D., F.R.S.
Alfred S. Taylor, M.D., F.R.S.
Charles Tomlinson, Esq.
Robert Warington, F.C.S.
A. W. Williamson, Ph.D., F.C.S.

## Treasurer.

Henry Beaumont Leeson, M.D., F.R.S., St. Thomas's Hospital.

## Secretary.

Theophilus Redwood, Esq., 19, Montague Street, Russell Square.


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The Cavendish Society was instituted for the promotion of Chemistry and its allied sciences, by the diffusion of the literature of these subjects. The Society effects its object by the translation of recent works and papers of merit; by the publication of valuable original works which would not otherwise be printed, from the slender chance of their meeting with a remunerative sale; and by the occasional republication or translation of such ancient or earlier

modern works as may be considered interesting or useful to the Members of the Society. The publications and other business of the Society are conducted by the Council, who, with other officers, are elected by ballot at a General Meeting of the Society held on the 1st of March of each year.

Members are admitted on application to the General or Local Secretaries, and contribute an Annual Subscription of one guinea, which entitles them to a copy of every work published by the Society for the period during which their membership continues. The number of works thus published will necessarily depend on the number of subscriptions, but will not be less than two octavo volumes for each year. These works are handsomely printed, on a uniform plan, for Members only.

The following are the books issued for the years specified:—

1848.

1.—CHEMICAL REPORTS AND MEMOIRS. Edited by Thomas Graham, F.R.S. (Out of Print.)

2.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Translated by Henry Watts, B.A., F.C.S. Vol. I.

1849.

3.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. II.

4.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. III.

5.—THE LIFE AND WORKS OF CAVENDISH. By Dr. George Wilson.

1850.

6.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. IV.

7.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. V.

1851.

8.—PHYSIOLOGICAL CHEMISTRY. By Professor Lehmann. Translated by George E. Day, M.D., F.R.S. Vol. I.

9.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. VI.

The sixth volume of Gmelin's Hand-Book of Chemistry, which will be ready by the end of the present year (1851), concludes the Inorganic part of this work. The part relating to Organic Chemistry will be immediately proceeded with.

The first of the Society's publications, the volume of Chemical Reports and Memoirs, being out of print, those who now join the Society, and desire to obtain the whole of Gmelin's Chemistry, are supplied with the first volume on payment of half the subscription for 1848. In anticipation of a continued demand, by new members of the Society, for all the volumes of Gmelin's standard work, a larger number was printed than was immediately required, and copies still remain on hand.

Among the works which are either now in progress, or for the publication of which arrangements are being made, are—

The second and third volumes of LEHMANN's Physiological Chemistry, translated by DR. DAY.

The Hand-Book of Chemistry, by LEOPOLD GMELIN. (Organic Chemistry.)

BISCHOF's Elements of Chemical and Physical Geology.

The Essays of SAUSSURE, together with abstracts of the works of HALES, INGENHOUSZ, SENNEBIER, WIEGMANN, and other contemporaneous writers on the Chemistry of Vegetation.

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The Council do not undertake to defray the expense of conveying books to those Members not resident in the Metropolis, excepting where several volumes can be sent together in a parcel; and even in those cases it is hoped that Members will promote an economical arrangement, whenever practicable, by having the books sent in booksellers' parcels, or otherwise, free of charge.

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